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VII.—ABNORMAL, BIOCHEMICAL PRODUCTS OF THE RUE ANEMONE.

BY FREDERICK S. BEATTIE.

During certain investigations into the flora of northeastern Rhode Island, a new phase of the subject of plant life and its chemical products came into prominence. Vegetable growths form a fairly important source of numerous chemical compounds, of which some few have from time to time been obtained synthetically, but of which the greater part still offers subjects for exhaustive investigation. The case in question differs from that of such compounds, in that it relates to bodies which so far have been regarded as purely synthetic, but which now appear in the light of substances also occurring naturally.

The plant known variously as *Syndesmon thalictroides* Hoffmg., *Anemonella thalictroides* Späth, and *Thalictrum anemonoides* Michx., which is commonly known as rue anemone, in its normal condition, as far as the author has been able to examine it, contains no cyclic compounds, either with or without nuclear nitrogen; the nitrogenous content is exceedingly small, too small, in fact, for satisfactory estimation;

and the major content of the dry plant, beside vascular tissue, is apparently starch, chlorophyll, and some vegetable albuminous matter. The material under consideration consisted of the above-mentioned species; not in normal condition, but showing marked fasciation.¹ The species in this condition was found, in point of life products, to depart in noteworthy degree from the normal, containing a high percentage of quinoline derivatives. Fuller mention of the details of this departure will be made after the investigation of the products in question has been described.

EXPERIMENTAL.

Extraction and Separation of the Biochemical Products.—Two hundred and thirty grams of the finely cut plants, dried at 120°, were extracted repeatedly with boiling dried ether, and the ethereal extract subjected to distillation from the water bath. A gray, crystalline residue was obtained, weighing 38.7 grams. This was dissolved in 200 cc. boiling absolute ether, filtered hot to remove a small quantity of a blackish impurity, and cooled. Small, colorless crystals were deposited sparingly. After one-half hour, as their quantity did not increase perceptibly, the mixture was filtered, the crystals washed with a little cold absolute ether, and dried. They were thus obtained as small white leaves, weighing 5.3 grams and melting at about 250°. The ethereal filtrate was evaporated to crystallization, whereby a mass of fine white needles was obtained, weighing 32.4 grams and melting at 88°. The substances, therefore, were clearly different. As the high melting body was found to be somewhat soluble in hot acetone, the ground plants, already extracted with ether, were now exhausted with boiling acetone, and this extract distilled from the water bath as before. A further amount of the high melting substance, weight 8.1 grams, was thus obtained in small white leaves melting at 251°. Further extraction of the residue with benzene, chloroform, ethyl and methyl alcohol, and ligroin, gave nothing. The two lots of the sub-

¹ A pathological condition in which the malformed plant displays a flattening or lateral compression of parts which are in cross section usually circular; e. g., the stem, tubers, ovaries.

stance melting at about 250° were treated separately with dilute sodium carbonate solution and with dilute ammonia water, in which they dissolved easily. A neutral solution of the substance in ammonia water gave a white precipitate with silver nitrate. As the substance appeared to be an acid, it will be referred to hereafter as the high melting acid, and taken up later in this paper. The body which melted at about 88° did not dissolve in dilute sodium carbonate or ammonia water, neither did it dissolve rapidly in a 10 per cent solution of caustic soda. It will therefore be designated temporarily as the neutral substance.

Purification and Properties of the Neutral Substance.—The major part of the extracted compounds, which was obtained by evaporation of the ethereal filtrate, melted at 88° – 89° . It was recrystallized several times from a mixture of three volumes acetone and one volume water, this mixture being found to give better results than either ether or pure acetone. After one recrystallization the melting point rose to $93^{\circ}.0$; after the second, it was $93^{\circ}.4$, at which it remained after three more recrystallizations. From the original 32.4 grams were thus obtained 29.7 grams of the purified product. Evaporation *in vacuo* below 80° of filtrates from these recrystallizations gave a thick yellow oil weighing 2.6 grams, nonvolatile with steam, not solidifying in a freezing mixture, and resinifying after standing two weeks in a stoppered bottle.

The neutral substance, thus purified, dissolved very easily in absolute and 96 per cent alcohol, easily in acetone, ether, benzene, moderately in glacial acetic acid, but not at all in hot or cold water. It possessed a peculiar, very fragrant and persistent odor, somewhat like that of the yellow melilot. From dilute acetone it crystallized in shining white needles, 3–4 mm. long. Qualitative analysis showed that the substance contained nitrogen, but no sulphur. Burned on platinum foil, it left no ash.

I. 0.2314 gram gave 13.4 cc. N at $18^{\circ}.0$ C. and 756.2 mm.¹

¹ In this, as in all the other nitrogen determinations, the gas was measured over a 50 per cent solution of potassium hydroxide.

II. 0.3026 gram gave 0.7314 gram CO_2 and 0.1326 gram H_2O .

Molecular weight determinations by the freezing point method gave the following results:

	Acetic acid. Grams.	Substance. Gram.	Δ .	Mol. wt.
I.	10.0000	0.1687	0°.309	212
II.	10.0000	0.1423	0°.264	210
III.	10.0000	0.1946	0°.352	216

Mean, 213

It was impossible to calculate from these data a satisfactory formula for the substance, the formulae agreeing best with the results being $\text{C}_{11}\text{H}_9\text{NO}_3$, with a molecular weight of 203, and $\text{C}_{11}\text{H}_{10}\text{NO}_3$, with a molecular weight of 204. It was therefore thought advisable to obtain a better idea of the structure of the neutral substance, in the hope that some light might thereby be thrown upon the above difficulty.

Hydrolysis of the Neutral Substance.—The substance, dissolved in benzene, did not add bromine. On standing in the cold with dilute (5 per cent) aqueous potassium hydroxide it dissolved very slowly, without evolution of gas. The solution thereby obtained was clear, colorless, odorless; on acidification with hydrochloric acid it gave a copious white precipitate, which, with much excess of acid, redissolved slowly. This acid solution was made alkaline with 10 per cent caustic potash, and dilute hydrochloric acid added cautiously till precipitation was complete. The filtered and washed precipitate dissolved very readily in dilute caustic alkalis, and in alkaline carbonates with evolution of carbon dioxide. Ten grams of the neutral substance were therefore hydrolyzed by warming at 90° with a solution of 10 grams caustic potash in 200 cc. water, the mixture being heated on the water bath under a return condenser, with almost continuous shaking. The substance melted in contact with water below 80° , although its proper melting point was over 90° . After being heated and shaken twenty minutes, the oily layer had disappeared entirely, and the solution was

clear. As it was suspected that the neutral substance might be an ester, the condenser was now reversed, and the mixture heated to gentle boiling over a small flame until 30 cc. had distilled over. This distillate will be taken up later. The liquid remaining in the flask was now cooled, and treated carefully with dilute hydrochloric acid. A white precipitate was obtained as before, which, after standing one-half hour, was filtered, washed, and dried. Its weight (crude) was 9.21 grams: recrystallized three times from acetone, it was obtained in the form of silky, white needles, weighing 8.79 grams. From its behavior toward alkalis it was clearly an acid. It melted sharply at $319^{\circ}.4$, after three recrystallizations and after repeated solution in soda solution and subsequent precipitation therefrom by hydrochloric acid. On melting, it became brown, and gave off bubbles of gas. Heated slowly, it sublimed below its melting point. It dissolved sparingly in hot alcohol, ether, benzene, and chloroform, rather easily in hot acetone and glacial acetic acid, not at all in hot water.

I. 0.3293 gram gave 20.4 cc. N at 17° .1 and 759.6 mm.

II. 0.1823 gram gave 0.4244 gram CO_2 and 0.0608 gram H_2O .

III. 0.1989 gram gave 0.4627 gram CO_2 and 0.0666 gram H_2O .

Molecular weight determinations by the freezing point method gave the following results:

	Acetic acid. Grams.	Substance. Gram.	Δ .	Mol. wt.
I.	10.0000	0.1821	$0^{\circ}.388$	183
II.	10.0000	0.1249	$0^{\circ}.255$	191
				Mean, 187

The values obtained approximate very closely to the formula $\text{C}_{10}\text{H}_7\text{NO}_3$, which has a molecular weight of 189.

	Calculated for $\text{C}_{10}\text{H}_7\text{NO}_3$.	I.	Found.	II.
C	63.49	63.49	63.44	
H	3.70	3.71	3.72	
N	7.41	7.34		

About 0.5 gram was converted into the barium salt by treatment with water and careful addition of barium hydroxide solution, phenolphthalein being used as the indicator. The solution was then concentrated to a small bulk and the colorless crystals which separated abundantly were filtered, recrystallized once from hot water, in which the salt was sparingly soluble, and dried at 110° to constant weight.

0.4826 gram salt gave 0.2186 gram BaSO_4 .

	Calculated for $\text{C}_{10}\text{H}_7\text{N}_2\text{O}_8\text{Ba}$.	Found.
Ba	12.91	12.86

The lead salt was prepared by mixing a neutral solution of the acid in ammonia water with lead acetate solution. It was obtained as a white, amorphous powder, insoluble in water. It was not analyzed.

Thermolysis of the Acid $\text{C}_{10}\text{H}_7\text{NO}_3$ to the Base $\text{C}_6\text{H}_7\text{NO}$.—As it had already been noticed that the acid, when fusing, gave off a gas, attention was next turned to this point. By careful fusion of a small quantity of the acid, the gas formed was proved, by testing with baryta water, to be carbon dioxide. Three and four-hundredths grams were then heated carefully in a tared flask, in a current of hydrogen, to 320° , and then to 325° , where the temperature was maintained for half an hour, tests being made from time to time for the presence of carbon dioxide in the escaping hydrogen. Nearly all the carbon dioxide was expelled in the first ten minutes, entirely so in twenty minutes. The reaction product was then allowed to cool, still in an atmosphere of hydrogen. The product solidified on cooling to a pale brown, crystalline mass, weighing 2.12 grams. Recrystallized from benzene it was obtained in white, glistening needles, which after three recrystallizations melted constantly and sharply at $208^{\circ}.5$. As a qualitative examination showed the presence of nitrogen, the substance was analyzed, with the following results:

I. 0.2817 gram gave 23.1 cc. N at $20^{\circ}.0\text{ C.}$ and 760.4 mm.

II. 0.1879 gram gave 0.5129 gram CO_2 and 0.0824 gram H_2O .

III. 0.2006 gram gave 0.5478 gram CO_2 and 0.0901 gram H_2O .

The compound was clearly a base, as it dissolved easily in the halogen acids, also in sulphuric and nitric acids, all dilute. It was not possible to obtain salts in this manner. The hydrochloride was obtained as a white crystalline powder by passing dry hydrochloric acid gas into a saturated solution of the base in benzene. The crystals, dried *in vacuo* over caustic soda, gave, on analysis, the following result:

0.2166 gram gave 0.1697 gram AgCl = 0.0432 gram HCl .

On the assumption that the substance in question is a monacid base, the molecular weight of the hydrochloride would be 183, and that of the base alone would be 146.

On addition of platinic chloride solution to a rather strong solution of the base in hydrochloric acid, the chloroplatinate was precipitated as a yellow crystalline powder. This was filtered off, washed with cold water, in which it was only sparingly soluble, and dried *in vacuo* over sulphuric acid. Analyzed for platinum, it gave the following:

0.6128 gram gave 0.1706 gram Pt.

The molecular weight of the chloroplatinate is therefore 700, of the base, 145, which agrees well with the provisional 146 given above. From the data now in hand, the formula of the base is $\text{C}_9\text{H}_7\text{NO}$.

	Calculated for $\text{C}_9\text{H}_7\text{NO}$	I.	Found.	II.
C	74.48	74.44		74.47
H	4.83	4.87		4.99
N	9.65	9.63		

Reduction of the Base $\text{C}_9\text{H}_7\text{NO}$ to Isoquinoline.—It was seen at once that this formula was that of an oxyquinoline; furthermore, the melting point, 208° , agreed exactly with that assigned to 1-oxyisoquinoline. About 3 grams, prepared as before by fusing the acid $\text{C}_{10}\text{H}_7\text{NO}_3$ in an atmosphere of hydrogen, were distilled with excess of zinc dust and pumice from a hard glass tube, in a current of hydrogen. A yield of about 40 per cent was obtained of a pale yellow oil, which, when

frozen and pressed out upon cold porous porcelain, appeared in a colorless, crystalline condition, melting sharply at $24^{\circ}.5$, and boiling, as far as could be determined from the small quantity at the author's disposal, at about 235° – 237° . The melting and boiling points of isoquinoline are given as $24^{\circ}.6$ and $240^{\circ}.5$, respectively. In order to confirm the identity of the substance, a solution of the hydrochloride of the base (clearly a base, as it dissolved readily in dilute mineral acids, and not at all in even concentrated caustic alkalis) was precipitated with strong platinic chloride solution. The chloroplatinate thus formed, when recrystallized from hot water, was obtained as a mass of fine yellow needles of a decided reddish tinge, melting sharply at 263° with decomposition.

0.5612 gram of salt dried *in vacuo* gave 0.1552 gram Pt.

	Calculated for $(C_9H_7N.HCl)_2PtCl_4.2H_2O$.	Found.
Pt	27.67	27.65

0.4091 gram of salt dried at 170° gave 0.1186 gram Pt.

	Calculated for $(C_9H_7N.HCl)_2PtCl_4$.	Found.
Pt	27.19	28.99

The molecular weight of the base is therefore about 131. That of isoquinoline is 129.

The picrate of the base formed yellow needles, rather difficultly soluble in cold absolute alcohol. It melted at 221° – 222° . Isoquinoline picrate melts at 222° – 223° .

The sulphate was prepared by adding sulphuric acid (1 mol.) dissolved in ether, to a solution of the base (1 mol.) in absolute alcohol, and evaporating to crystallization. So prepared, it formed small, white, shining leaves, moderately soluble in hot, more difficultly in cold, alcohol. The vacuum dried salt, on analysis, gave the following result:

0.4447 gram gave 0.4549 gram $BaSO_4$.

	Calculated for $C_9H_7N.H_2SO_4$.	Found.
S	14.09	13.76

Constitution of the Acid $C_{10}H_7NO_3$.—From the experimental data now at hand, the relationship of the acid $C_{10}H_7NO_3$,

derived by hydrolysis from the neutral body, to the base isoquinoline becomes clearer. As on fusion it passes over, with loss of carbon dioxide, to oxyisoquinoline, or isocarbostyryl, it is clearly a carbonic acid of oxyisoquinoline, and, as the analyses show, a monobasic acid. There is no hesitation in designating it as 1-oxyisoquinoline-3-carboxylic acid or isocarbostyryl-3-carboxylic acid, as the melting point, 320°, agrees exactly with that given in the literature.

Study of the Aqueous Distillate from Hydrolysis.—The 30 cc. of distillate obtained from the potassium hydroxide hydrolysis of the neutral body were united with a second 30 cc. obtained similarly from hydrolysis of another 10 gram lot of the neutral body, and the mixture was fractionated repeatedly with great care. After nine fractionations through a small Hempel column, the products resolved themselves into three parts; a fraction boiling constantly at 66°–67°, weighing 0.8 gram, one boiling at 75°–80°, weighing 0.7 gram, and the residue, boiling constantly at 100°, weighing about 56 grams. The two lower boiling fractions possessed characteristic alcoholic odors. Both responded to the iodoform test, the 66°–67° fraction yielding traces only, the 75°–80° fraction giving iodoform abundantly. They were identified as methyl alcohol and ethyl alcohol, respectively, by conversion into esters of paranitrocinnamic acid, of known melting point. It was intended to prepare their esters with *s*-trinitrobenzoic acid, but the *s*-trinitrobenzoyl chloride destined for that purpose was lost by an accident, and as no more trinitrobenzoic acid was at hand, recourse was had to paranitrocinnamyl chloride. The lower boiling fraction, 0.32 gram (1 mol. calculated for CH_3OH), was treated with 2.12 grams (1 mol.) of phosphorus pentachloride, with cooling; the reaction product was then heated at 100° for ten minutes to complete the reaction, cooled, and treated with ice water. A white, crystalline solid was precipitated, which was filtered off, washed well, and dried. It melted at 159° C. Recrystallized twice from pure acetic ester, it melted constantly at 161°.3. The melting point of paranitrocinnamic methyl ester is 161° C. Forty-six hundredths gram of the higher boiling

fraction (1 mol. calculated for C_2H_5OH), was treated similarly with 2.12 grams (1 mol.) of phosphorus pentachloride. The product in this case was a crystalline, slightly yellowish powder, which melted at 135° – 136° . Three recrystallizations afforded a pale yellow ester which melted constantly at $138^\circ.4$ C., the melting point of paranitrocinnamic ethyl ester being $138^\circ.5$.

Identity of the Neutral Substance.—The neutral body, in view of the results already obtained, is evidently a mixture of esters of 1-oxyisoquinolinecarboxylic acid since on heating with aqueous potassium hydroxide it splits up into the acid just mentioned and at least two well identified alcohols, methyl and ethyl. Analysis of the neutral substance, which may now be called the ester mixture, gave values which it was difficult to reconcile with any particular formula. The methyl and the ethyl ester of the oxyisoquinoline acid would give the following values (the analysis of the ester mixture being subjoined):

	Calculated for methyl ester.	Calculated for ethyl ester.	Found for ester mixture.
C	65.04	66.36	65.92
H	4.43	5.07	4.87
N	6.89	6.45	6.81

By inspection, it will be seen that the figures actually obtained are what might be expected from a mixture of the two esters. It was not found possible, with the limited amount of mixture remaining, to effect a separation of the esters by crystallization, nor even so to alter their relative proportions as to change the melting point of the mixture. Such cases are hardly infrequent, *e. g.*, the nitrobenzaldehydes, ortho and meta. That the two esters were at least present in, if not entirely constituting, the ester mixture has already been made clear.

Study of the High Melting Acid.—The two portions of the high melting acid, weighing together 13.4 grams, were recrystallized from acetone-ether. After one recrystallization they melted at 253° ; after the second, at $254^\circ.3$; subsequent recrystallizations failed to alter the melting point.

The acid dissolved somewhat in both hot ether and hot acetone; in cold ether it was insoluble, in cold acetone difficultly soluble; easily soluble in hot, less so in cold, alcohol. Qualitative examination showed nitrogen to be present, sulphur to be absent. Burned on platinum it gave no residue. Analysis gave the following:

- I. 0.1604 gram gave 10.21 cc. N at 19°.2 C. and 761.4 mm.
 II. 0.1733 gram gave 0.4485 gram CO₂ and 0.0851 gram H₂O.

Determinations of the molecular weight gave the following values:

	Phenol. Gram.	Substance. Gram.	Δ.	Mol. wt.
I.	12.0071	0.1620	0°.541	187
II.	12.0071	0.1413	0°.474	186
Mean,				186.5

According to these data the formula of the acid would be C₁₁H₉NO₂, the molecular weight of which, 187, is almost exactly that found.

	Calculated for C ₁₁ H ₉ NO ₂ .	Found.
C	70.59	70.05
H	4.81	4.81
N	7.48	7.50

The silver salt was prepared by mixing a neutral solution of the acid in ammonia water with silver nitrate solution, and was obtained as a white, granular precipitate. After being well washed and dried *in vacuo*, it was analyzed for silver with the following results:

0.2181 gram gave 0.0799 gram Ag.

	Calculated for C ₁₁ H ₉ NO ₂ Ag.	Found.
Ag	36.73	36.66

Base from the Acid C₁₁H₉NO₂.—The persistent presence of nitrogen in this, as well as in the other compounds studied, led the author to believe that this body also was a heterocyclic compound referable finally to quinoline. The preparation of the parent hydrocarbon confirmed this belief.

Approximately equal weights of the barium salt of the acid and of barium hydroxide, both thoroughly dried, were distilled rapidly from a hard glass tube through which was passed a current of hydrogen. About 65 per cent of an oil came over, which possessed a pale yellow color and characteristic quinoline odor. On being strongly cooled, it solidified; after being pressed out in that condition upon cold porous porcelain, it was found to melt at 9° – 12° , and to boil above 240° . It dissolved readily in dilute mineral acids, not at all in even concentrated caustic alkalies, and was therefore of basic nature. It contained nitrogen. The analysis follows:

I. 0.2007 gram gave 16.72 cc. N at 20° .0 C. and 760.6 mm.

II. 0.1623 gram gave 0.4991 gram CO_2 and 0.0922 gram H_2O .

III. 0.0989 gram gave 0.3039 gram CO_2 and 0.0564 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_9\text{N}$	I.	Found.	II.
C	83.91	83.87		83.82
H	6.29	6.31		6.33
N	9.79	9.78		

The chloroplatinate was prepared in the usual manner. As it evidently contained water of crystallization, it was dried to constant weight at 140° . On analysis,

0.4067 gram gave 0.1178 gram Pt.

This gives the molecular weight of the base as 132, which agrees moderately well with 143, the value derived from the combustions. The formula of the base is therefore $\text{C}_{10}\text{H}_9\text{N}$, which is that of a methylquinoline or methylisoquinoline. The picrate and the iodomethylate of the base were prepared, with the hope of obtaining some evidence as to the nature of the base. The picrate melted sharply at 187° . The iodomethylate, prepared by heating equal weights of base and methyl iodide in a sealed tube at 80° for two hours, was obtained as a yellow crystalline deposit, which, pressed out upon porcelain and recrystallized from absolute alcohol, melted constantly at 221° . The melting point of these two

characteristic derivatives indicate that the base is *py*-3-methylquinoline, and that the high melting acid must be a carboxyl derivative of that hydrocarbon. The melting point, 254°, agrees with that given by Miller¹ for *py*-3-methylquinoline-4-carboxylic acid. Its identity as such is confirmed by the fact that the only other known methylquinoline-carboxylic acid, which is derived from *py*-2-methylquinoline, namely the 3,2-acid, melts at 144°, and decomposes at 160° into carbon dioxide and its parent base, which the acid in question did not do of itself even at 260°. Miller states that the 3-methylquinolinecarboxylic acid is insoluble in ether. The author has found it to be rather sparingly soluble in boiling ether, but insoluble in even warm ether. In all other points his acid agrees with Miller's.

Conclusion.

The summary may be briefly stated thus: In fasciated plants of the species *Syndesmon thalictroides* Hoffmg. were found 1-oxyisoquinoline-3-carboxylic acid, in the form of its methyl and ethyl esters, and *py*-3-methylquinoline-4-carboxylic acid in the free state. The occurrence of these compounds here is of peculiar interest for three reasons:

(1) The two acids have been regarded, to the present, as purely synthetic products, and now appear for the first time as biochemical products.

(2) The biosynthesis of these two acids, as well as of other compounds of like nature, by this species, either normal or abnormal, has been heretofore unobserved.

(3) The percentage of the products investigated is astonishingly high: about 20 per cent of the dry plant.

No mention exists in the literature, as far as I can find, of investigations in the *Ranunculaceae* of this section.

All plants from which the material studied was derived were fasciated to an extreme degree, and constituted a sharply defined colony. Experiments performed with normal plants from the same wooded slope, within fifty feet of the fasciated colony, and living under exactly the same conditions of

¹ Ber. d. chem. Ges., 23, 2257.

moisture, shade, drainage, etc., afforded no trace of the compounds obtained from the diseased plants. The soil throughout the whole tract under inspection was of uniform quality, the percentage of nitrogen in specimens of soil taken at random from seventeen spots within the said tract, and dried at 110° , ranging from 0.86 to 0.92 per cent.

It would be tempting to speculate upon possible explanations; but sufficient experimental data are not at hand to justify one in doing so. Experiments made later by the author seem to indicate that the substances which form the subject of this investigation were coincident, but not necessarily concomitant, with pronounced fasciation of the species. Results already obtained with diseased specimens of another species make it clear that abnormal chemical products often do accompany grave physical malformations; but more than this one cannot at present venture to say.

Work of similar nature, involving other species of the northeastern United States, is being carried on by the author.

SOUTH BETHLEHEM, PENNA.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND CINNAMYLIDENE ESTERS.

II. REACTIONS WITH METHYL α -PHENYL CINNAMYLIDENEACETATE.

BY MARIE REIMER AND GRACE POTTER REYNOLDS.

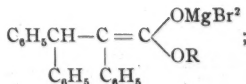
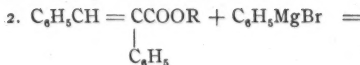
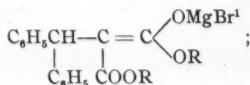
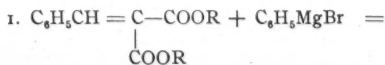
In a previous paper¹ it was shown that the reaction between Grignard's reagent and methyl cinnamylidenemalonate consists entirely in 1,4 addition. It was pointed out that the course of the reaction was undoubtedly influenced by the carboxyl group in the α position, as negative groups in this position are known to increase the tendency toward 1,4 addition. In continuing the study of cinnamylidene esters, with a view to

¹ THIS JOURNAL, 38, 227.

determining the influence of the second ethylene linkage on the reactivity of the conjugated system, $C=C-O$, the next ester to be studied was methyl α -phenylcinnamylideneacetate, which differs from the malonate only in having the less negative phenyl group in the α position.

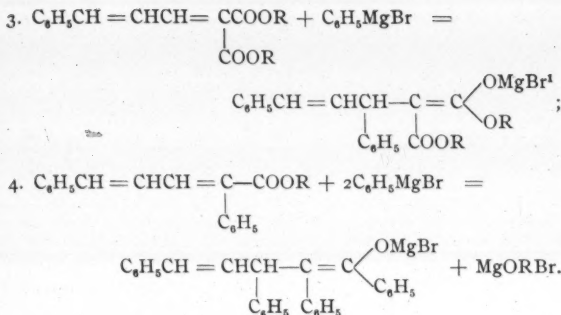
The results with this ester differ widely from those with the malonate and also from those with the corresponding benzylidene esters. Under conditions which are usually favorable for the reaction between Grignard's reagent and unsaturated esters, the reaction in this case does not take place at all or only to a very slight extent. When the ester is added to a large excess of the magnesium compound at the temperature of boiling ether, it is possible to bring about a reaction but the yield of product is never quantitative. The resulting compounds are not esters, formed by 1,4 addition, but ketones or tertiary alcohols formed by replacement of the methoxyl group and subsequent addition of a second molecule of reagent in the 1,4 or 1,2 position, according to the nature of the magnesium compound.

The reactions between phenylmagnesium bromide and the corresponding benzylidene and cinnamylidene esters are as follows:



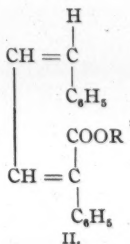
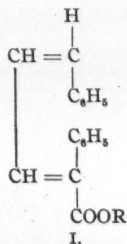
¹ Kohler: *THIS JOURNAL*, **34**, 132.

² Kohler and Heritage: *Ibid.*, **33**, 153.



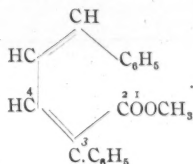
Of the above reactions the first three take place smoothly under a variety of conditions. The entire product is formed by 1,4 addition. The fourth reaction does not take place readily. The product consists of 87 per cent ketone, formed by replacement of the OR group and addition of a second molecule of the reagent in the 1,4 position to the ketone thus formed. In view of the similarity between reactions (1) and (2), it is not probable that the difference between reactions (3) and (4) is due entirely to the chemical nature of the α substituent.

A possible explanation for the great unreactivity of α -phenylcinnamylideneacetate may be found in a consideration of the spatial arrangement of the molecule. The possible configurations of the ester molecule are

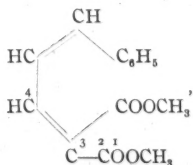


¹ Loc. cit.

and the two isomers in which the hydrogen of the benzal group is in the vicinity of the phenyl or the ester group. Of the compounds I. and II., the second would be more stable as the negative phenyl group is in the neighborhood of the more positive —COOCH_3 group.¹ If the molecule has this configuration, the ester group would be protected in a way analogous to that of a diortho substituted ester, as may be seen by the formula



If the formula of this ester is compared with that of methyl cinnamylidenemalonate,



it is seen that the possibility of steric hindrance does not arise in the latter case. Only one of the ester groups enters into reaction and one of these is free to react, no matter what the spatial arrangement of the molecule is. Experiments have shown that there is, in fact, no hindrance, the reaction taking place smoothly at 0° .

A further substantiation of this view is found, in the case of the two isomeric methyl cinnamylideneacetates, in which hydrogen is present in place of the α -phenyl group. Preliminary experiments have shown that these esters react readily with Grignard's reagent at -15° .

It was also found that whereas methyl- and phenylmagnesium halides react with the α -phenyl ester under favorable

¹ Cf. Stoermer and Frederici: Ber. d. chem. Ges., 41, 324.

conditions, giving comparatively large yields, benzylmagnesium bromide gives but a 17 per cent yield, and still larger molecules, such as naphthyl- and *o*-tolylmagnesium bromide, gave too small a quantity of reaction product to be isolated.

It is possible that, with the aromatic magnesium compounds, 1,4 addition to the ester in question takes place to a small extent, but the speed of the replacement reaction, under conditions which are necessary in order that a reaction may take place at all, is so much greater than that of the addition reaction that the final product is practically entirely ketone formed by replacement of the methoxyl group and subsequent addition of a second molecule of the reagent.

EXPERIMENTAL.

The α -phenylcinnamylideneacetic acid used was prepared by the method of Thiele.¹ It was found possible to purify the acid quickly and satisfactorily as follows: The crude acid was dissolved in a hot, concentrated solution of sodium carbonate from which, on cooling, the sodium salt separated in glistening yellow plates. The salt was filtered, dried, and then purified by being vigorously shaken with ether in a large flask. The ethereal extract contained hydrocarbon, formed by decomposition of part of the acid, and a very small quantity of sodium salt. The acid was precipitated from a concentrated solution of the purified salt. An 83 per cent yield of acid, pure after one crystallization from alcohol, was obtained.

The methyl ester was prepared according to the directions of Michael and Leighton.²

Reaction with Phenylmagnesium Bromide. α,β -Diphenyl- γ -benzylbutyrylphenone, $C_6H_5CH=CHCH-CHCOC_6H_5$.—An ethereal



solution containing 7 grams (1 mol.) of phenylmagnesium bromide was slowly added to an ethereal solution of 14 grams (1 mol.) of the methyl ester cooled to -10° , and the mixture

¹ Ann. Chem. (Liebig), 306, 197.

² J. prakt. Chem. [2], 88, 521.

kept at that temperature for one hour. The product was treated with iced hydrochloric acid and the ethereal extract dried over calcium chloride. On evaporating, over 13 grams of the original ester crystallized out. There had been, therefore, practically no reaction.

The experiment was repeated at 0° with the same proportions of reagents and the mixture allowed to stand 15 hours at room temperature. Twelve and a half grams of ester were recovered.

When the proportions of ester to magnesium compound were 1 : 2 and the ester was added to the reagent a reaction took place at 0° , a very small quantity of a white crystalline solid separating from the ethereal solution after decomposition of the reaction product with ice and hydrochloric acid. This was subsequently proved to be a ketone formed by replacement of the methoxyl group and addition of a second molecule of reagent in the 1,4 position. After complete evaporation of the ether a brown, pasty mass remained. This was boiled with alcoholic potash for two hours, the alcohol evaporated, and the residue extracted repeatedly with water. From the aqueous solution hydrochloric acid precipitated an acid in a very impure condition. It was necessary to recrystallize this acid from alcohol and water a great many times before it was pure enough for identification. It was then found to be α -phenylcinnamylideneacetic acid, formed by hydrolysis of the original ester which had not entered into reaction with the Grignard's reagent. The fact that the acid was so extremely hard to purify makes it probable that a small quantity of some other acid, possibly formed by 1,4 addition to the ester, was present. No such compound could, however, be isolated.

The reaction was carried out in boiling benzene but the results were unsatisfactory.

The ketone mentioned above was the only product of reaction which could be isolated. To obtain the best yield of this compound the following procedure was adopted: An ethereal solution containing 1 molecule of ester was added very slowly to a boiling ethereal solution containing at least 3 molecules of phenylmagnesium bromide and the mixture boiled for two

hours. After decomposition in the usual way the ethereal extract was dried and the ether entirely evaporated. The oily product was suspended in alcohol, excess of alcoholic potash added, and the mixture boiled for one hour to remove any unchanged ester. The alcohol was then evaporated off, the solid residue extracted several times with water, and dried in a current of air. From the aqueous extract only a trace of original acid was obtained.

The solid product was purified by crystallization from a mixture of chloroform and alcohol. Analyses and subsequent reactions proved the substance to be α,β -diphenyl- γ -benzal-butyrophenone.

Analysis:

0.1508 gram substance gave 0.4966 gram CO_2 and 0.0877 gram H_2O .

	Calculated for $\text{C}_{29}\text{H}_{24}\text{O}$.	Found.
C	89.69	89.81
H	6.18	6.46

Molecular weight determined in boiling benzene. $K = 26.1$.

Weight solvent.	Weight substance.	Elevation of boiling point.	Molecular weight.
51.1100 grams	0.3764 gram	0°.050	384
	0.5700 "	0°.073	398
	0.6962 "	0°.093	382
Average,			388
Calculated,			388

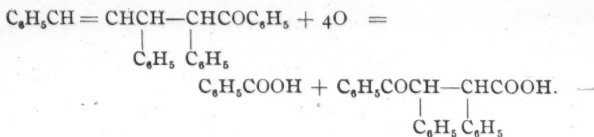
The compound is readily soluble in acetone, chloroform, and benzene, fairly soluble in ligroin and boiling alcohol, very slightly soluble in ether, insoluble in water. It separates from a mixture of chloroform and alcohol in very fine, soft, white needles, melting at $191^\circ.5$ – $192^\circ.5$. The purest product is obtained by crystallization from boiling alcohol, but the process is tedious for purification of a large quantity, as a liter of boiling alcohol is necessary to dissolve five grams of ketone. The substance dissolves slowly in concentrated sulphuric acid from

which it may be precipitated by water. The solution in sulphuric acid is a pale, salmon pink in color.

α, β -Diphenyl- β -benzoylpropionic Acid, $\text{C}_6\text{H}_5\text{COCH}-\text{CHCOOH}$.



—This acid was obtained by oxidation of the ketone, thus proving the structure of the latter, the oxidation reaction taking place as follows:



Twelve grams of ketone were dissolved in acetone, and finely powdered potassium permanganate was added gradually, the solution being kept cool by running water. Decolorization of the permanganate took place slowly. It was necessary to leave the mixture standing with excess of permanganate for several days, with frequent shaking, to insure complete oxidation. The solution was then decolorized by sulphur dioxide and filtered. The precipitated manganese dioxide was washed with acetone and then extracted repeatedly with boiling water. From the aqueous solution hydrochloric acid precipitated a colorless acid. This was crystallized from boiling alcohol from which it separates in small, shining needles melting at $211^\circ-212^\circ$. When dried on the water bath alcohol is given off and the crystals become opaque. The presence of alcohol of crystallization was proved by the formation of iodoform when the vapor from the heated acid was passed into a solution of potassium carbonate containing iodine.

Analysis of the air dried acid:

0.1539 gram substance gave 0.4517 gram CO_2 and 0.0768 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{18}\text{O}_2 \cdot \text{C}_6\text{H}_5\text{OH}$.	Found.
C	80.00	80.04
H	5.45	5.54

0.3621 gram substance heated at 100° to constant weight lost 0.0444 gram.

Calculated for
1 mol. C_9H_9OH .

12.23

Found.

12.26

The acid is very readily soluble in chloroform, acetone, and ether, soluble in hot benzene and alcohol, slightly soluble in ligroin, insoluble in water. It dissolves readily in concentrated sulphuric acid. The color of the solution is at first a brilliant purple, changing during the course of half an hour to bright yellow and then to brown.

The aqueous filtrate from which this acid was precipitated was evaporated to small volume. On cooling, benzoic acid crystallized out.

From the acetone filtrate there was obtained by evaporation of the acetone a small quantity of a yellowish oil which partially solidified. The amount was too small for identification but the substance is possibly a decomposition product of the ketonic acid, as the yield of the latter was small. From 12 grams of ketone were obtained 5 grams of ketonic acid and 3.2 grams of benzoic acid, instead of the calculated 10.2 grams and 3.8 grams, respectively.

Methyl α,β -Diphenyl- β -benzoylpropionate,
 $C_6H_5COCH-CHCOOCH_3$.—Three grams of acid, dried at 100° ,



were dissolved in methyl alcohol and hydrochloric acid gas passed into the warmed solution for two hours. On cooling the solution the ester crystallized out in shining, stiff, white needles. After one crystallization from methyl alcohol it melted sharply at 159° .

Analysis:

0.1508 gram substance gave 0.4418 gram CO_2 and 0.0818 gram H_2O .

C
H

Calculated for
 $C_{20}H_{16}O_4$.

80.23

5.81

Found.

79.90

6.02

The ester is readily soluble in ether, alcohol, chloroform, and acetone, slightly soluble in boiling ligroin, insoluble in cold ligroin and water. It dissolves slowly in concentrated sulphuric acid. The solution has the same purple color as that of the ketonic acid and the colors change in the same way.

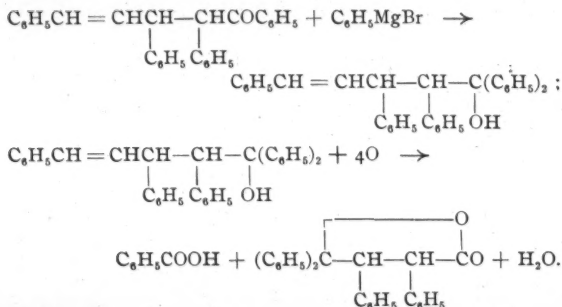
α,β -Diphenyl- γ -benzalbutyrophenone forms no oxime nor hydrazone. Five grams of the ketone in alcoholic solution were boiled with excess of potassium hydroxide and hydroxylamine hydrochloride for ten hours. The entire amount of ketone was regained unchanged. In this respect the ketone resembles benzpinacolone and other ketones in which the reactivity of the carbonyl oxygen is hindered by the groups in its immediate vicinity.

The same hindrance effect was noted when the ketone was treated with phenylhydrazine. No hydrazone was formed. This behavior is in accordance with the results obtained by Petrenko-Kritschenko and Eltschaninoff² and other investigators.

The ketone reacts readily, however, with Grignard's reagent. Thirteen and a half grams of ketone, suspended in absolute ether, were added slowly to a solution of phenylmagnesium bromide which contained 3 molecules of reagent for 1 of ketone. The reaction took place readily at 0° but, because of the relative insolubility of the ketone in ether, the reaction was usually carried out in boiling solution. After all the ketone had been added, the clear, rose colored solution was boiled for an hour and then decomposed in the usual way. After evaporation of the ether a heavy yellow oil remained. This was suspended in water and distilled with steam to remove a small quantity of diphenyl. The oil remaining in the flask could not be made to solidify under a variety of conditions. It decomposed when distilled under diminished pressure so that it was not possible to obtain it in pure condition. It was, therefore, oxidized. The oil was dissolved in acetone and treated with powdered potassium permanganate. The

Beckmann: Ann. Chem. (Liebig), **253**, 14.
Ann. Chem. (Liebig), **341**, 150.

reduction of the permanganate took place rapidly with considerable evolution of heat. The excess of permanganate was reduced with sulphur dioxide, and the precipitated manganese dioxide washed carefully with hot acetone. From the acetone solution a white, crystalline solid separated. It was purified by recrystallization from hot alcohol, from which it separates in fine needles, melting at 221° – $221^{\circ}.5$. Analyses and reactions show that the substance is a lactone formed by the loss of a molecule of water from the γ -oxy acid which results from the oxidation of the tertiary alcohol formed by the reaction of phenylmagnesium bromide on the ketone.



Analyses:

I. 0.1492 gram substance gave 0.4721 gram CO_2 and 0.0811 gram H_2O .

II. 0.1487 gram substance gave 0.4690 gram CO_2 and 0.0815 gram H_2O .

	Calculated for $\text{C}_{29}\text{H}_{29}\text{O}_2$	Found.	
		I.	II.
C	86.15	86.29	86.02
H	5.64	6.03	6.08

The lactone of γ -oxytetraphenylbutyric acid is soluble in ether, acetone, and chloroform, fairly soluble in hot benzene, ligroin, and alcohol. It is not affected by sodium carbonate solution but after long boiling in aqueous alcohol

which contains excess of potassium hydroxide it partially dissolves. When the alcohol is evaporated off and the aqueous solution acidified the lactone is precipitated.

The manganese dioxide precipitated during the oxidation was extracted with boiling water, and the filtrates concentrated by evaporation and acidified. A colorless acid was precipitated which, after one crystallization from water, melted sharply at 121° . It was pure benzoic acid.

A small quantity of a yellow oil was left after complete evaporation of the acetone from which the lactone had separated. It has a pleasant aromatic odor resembling that of diphenylmethane. The amount of the substance was too small to admit of purification and identification.

It is probable that the oil obtained as the product of the reaction between phenylmagnesium bromide and diphenylbenzalbutyrophenone is a mixture of a tertiary alcohol and its decomposition products, as it is to be expected that a substance of the composition of this alcohol would be a solid. When distilled under diminished pressure no water was given off and no constant boiling substance obtained. The distillate was a yellow oil from which crystals gradually separated. The substance was recrystallized from ligroin from which it separated in needles melting at 134° - 135° .

Analyses:

I. 0.1226 gram substance gave 0.3962 gram CO_2 and 0.0692 gram H_2O .

II. 0.1532 gram substance gave 0.4941 gram CO_2 and 0.0836 gram H_2O .

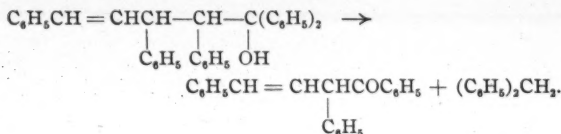
	Calculated for $\text{C}_{22}\text{H}_{18}\text{O}$.	I.	Found.	II.
C	88.59	88.13		87.96
H	6.04	6.27		6.06

The substance is readily soluble in benzene, chloroform, and alcohol, fairly soluble in ether and ligroin. It is unsaturated as it at once decolorizes a solution of potassium permanganate in the cold. Since benzoic acid is one of the products of oxidation the substance contains the group

$C_6H_5CH = CH$. No other acid product of oxidation was obtained.

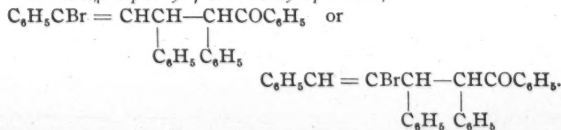
A small quantity of a yellowish oil was left after separation of the crystals from the distillate. This had a strong odor of diphenylmethane but was too small in quantity and too impure to be identified.

It is probable that the tertiary alcohol decomposes to a slight extent on formation and completely on distillation in the following way:



This ketone, phenylbenzalpropiofenone, has the composition $C_{22}H_{18}O$ and would give benzoic acid on oxidation. The other oxidation product, phenylbenzoylacetic acid, spontaneously decomposes so that no other acid product of oxidation would be obtained.

Brom- α,β -diphenyl- γ -benzalbutyrophenone,



—Three grams of diphenylbenzalbutyrophenone were dissolved in chloroform and one molecule of bromine in chloroform solution was added slowly. The temperature of the solution was kept at 0° . The bromine solution was decolorized as fast as added and fumes of hydrobromic acid were given off as soon as the reaction began. After all the bromine had been added, the chloroform was allowed to evaporate spontaneously. The colorless, crystalline product remaining was recrystallized from a mixture of chloroform and alcohol. After several recrystallizations, analyses showed that the substance was a mixture of a mono- and a dibrom-

ketone. It was, therefore, dissolved in chloroform and heated for some time on the water bath to decompose the dibrom compound. The product, on crystallization from chloroform and alcohol, separated in firm, white needles melting at 186° – 187° .

Analysis:

0.1536 gram substance gave 0.4201 gram CO_2 and 0.0711 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{18}\text{OBr}$.	Found.
C	74.50	74.57
H	4.92	5.14

The compound is readily soluble in benzene, acetone, chloroform, and ether, slightly soluble in alcohol, insoluble in water.

Attempts were made to determine the structure of the compound by oxidation. When the reaction was carried out under the conditions which are necessary for the oxidation of the original ketone the whole amount of the bromine compound was regained unchanged. When the mixture of bromine compound and excess of potassium permanganate in acetone solution was left standing ten days with frequent shaking, oxidation took place to a small extent. Some benzoic acid was obtained but a large part of the bromketone was regained. The great difference between the reactivity of the original ketone and the bromketone toward the oxidizing agent indicates that the bromine is attached to a doubly linked carbon atom. The fact that no odor of benzaldehyde was noticed during oxidation would point to the first rather than to the second formula given.

Reaction with Benzylmagnesium Bromide. α -Phenyl- β -benzyl- γ -benzalpropylbenzyl Ketone, $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}-\text{CHCOCH}_2\text{C}_6\text{H}_5$.



—The reaction was carried out under the conditions which gave the best yield of reaction product with phenylmagnesium bromide. Fifteen grams of ester were used. The oily product was suspended in water and distilled with steam to remove dibenzyl. The oil was then dissolved in alcohol and

boiled with excess of alcoholic potash for two hours to saponify any unchanged ester. From the aqueous extract of the product, hydrochloric acid precipitated ten grams of crude α -phenylcinnamylideneacetic acid. The residue, insoluble in water, was dissolved in hot alcohol from which it crystallized, on cooling, in fine white needles melting at 150° .

Analysis:

0.1229 gram substance gave 0.4025 gram CO_2 and 0.0780 gram H_2O .

	Calculated for — $\text{C}_{21}\text{H}_{22}\text{O}$.	Found.
C	89.42	89.31
H	6.73	7.05

The substance is very soluble in ether, chloroform, benzene, and ligroin, fairly soluble in alcohol, insoluble in water. It dissolves readily in concentrated sulphuric acid. The solution is a brilliant crimson color.

But 4 grams of crude ketone were obtained from 15 grams of ester, a 17 per cent yield.

Reaction with Orthotolylmagnesium Bromide.—The reaction was carried out as with the other reagents. From 15 grams of ester 10 grams of the corresponding acid were regained and 65 per cent of the orthotolylmagnesium bromide was regained as toluene. A small quantity of an oily substance was the only product of the reaction. From this no pure substance could be obtained.

Reaction with Naphthylmagnesium Bromide.—The reaction was carried out as before. From 20 grams of ester used 10 grams of acid were regained and 50 per cent of the naphthylmagnesium bromide was regained as naphthalene. As in the preceding case, no pure product could be obtained from the tarry substance formed, in small quantity, as a product of the reaction.

Reaction with Methylmagnesium Iodide.—When methylmagnesium iodide in ethereal solution was added to a solution of the ester in the same solvent, in a freezing mixture, at room temperature, or at the temperature of boiling ether, the whole amount of ester was regained. A reaction took place only

when excess of methylmagnesium iodide was present, the ester added to a solution of the reagent in boiling ether, and the reaction mixture boiled for some time.

Twenty-five grams of ester, dissolved in ether, were added slowly to a boiling solution containing 4 molecules of the reagent to 1 of ester. The solution was boiled for 10 hours and allowed to stand at room temperature for the same length of time. After decomposition of the magnesium compound and evaporation of the ether, the oily product was boiled for two hours with alcoholic potash. Less than 2 grams of crude acid, formed by saponification of unused ester, were obtained. The product of the reaction was a heavy reddish oil which could not be made to solidify. It was carefully washed, dried, and analyzed.

Analysis:

0.1918 gram substance gave 0.6368 gram CO_2 and 0.1325 gram H_2O .

	$\text{C}_{19}\text{H}_{19}\text{O}$.	Calculated for $\text{C}_{19}\text{H}_{18}$.	Found.
C	86.36	92.68	90.54
H	7.57	7.31	7.66

As the analysis gave results too high in carbon for a ketone or tertiary alcohol, it seemed probable that the compound was a mixture of tertiary alcohol and a hydrocarbon formed by loss of water from the alcohol. The presence of the hydroxyl group was proven by treating a solution of the oil with methylmagnesium iodide. There was a steady evolution of methane.

The oil was then distilled under diminished pressure. Water was split off and a yellow oil distilled over at $140^\circ\text{--}150^\circ$ (25 mm.). This oil was redistilled. From the distillate colorless, compact crystals gradually separated. These were washed with alcohol and crystallized from glacial acetic acid. From this solvent the compound separates in firm, white crystals, melting at $97^\circ\text{--}98^\circ$.

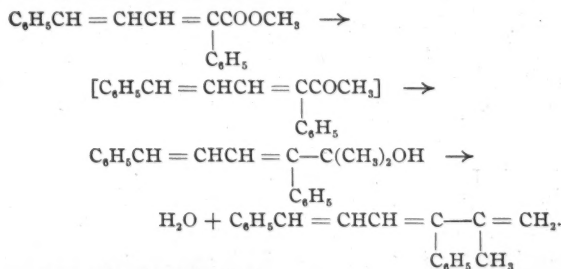
Analysis:

0.1027 gram substance gave 0.3471 gram CO_2 and 0.0700 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{18}$.	Found.
C	92.68	92.17
H	7.31	7.57

The hydrocarbon dissolves readily in ether, chloroform, acetone, and benzene, is moderately soluble in ligroin and glacial acetic acid, almost insoluble in cold alcohol, fairly soluble in hot alcohol, from which it separates in an oily condition.

The first product of the reaction is undoubtedly a ketone formed by replacement of the methoxyl group as in the reactions with phenyl- and benzylmagnesium halides. The ketone thus formed at once reacts with a second molecule of methylmagnesium iodide, the addition being to the carbonyl group, the usual reaction with methyl ketones. The tertiary alcohol thus formed easily loses water to form the unsaturated hydrocarbon:



CHEMICAL LABORATORY,
BARNARD COLLEGE,
July, 1908.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXI.—RESEARCHES ON PYRIMIDINES:
SYNTHESES OF SOME BENZYL DERIVATIVES
OF URACIL AND THYMINE.

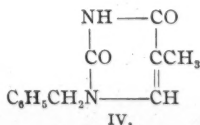
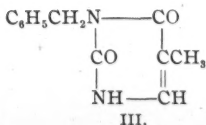
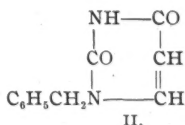
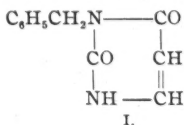
[THIRTY-EIGHTH PAPER.]

BY TREAT B. JOHNSON AND JOHN H. DERBY, JR.

In order to determine the structure of some new nitrogen derivatives of uracil and thymine it was essential to have knowledge of some characteristic nitrogen-alkyl derivatives of

these pyrimidines of known constitution. The only nitrogen-alkyl derivatives of uracil and thymine mentioned in the literature are 1,3-dimethylthymine¹ and the methyl and ethyl compounds, which have been described in previous papers from this laboratory.² These alkyl pyrimidines were not suitable for our work on account of their solubility, and difficulty of isolation when accompanied by impurities. Furthermore, 3-methyluracil has not been synthesized.

With the anticipation that the nitrogen-benzyl derivatives of uracil and thymine might be found to be more insoluble, and suitable for our work, we undertook this investigation. We shall describe in this paper the methods of preparation and the properties of 1-benzyluracil, I., 3-benzyluracil, II., 1-benzylthymine, III., and 3-benzylthymine, IV.



Johnson and Heyl³ showed that methyl iodide reacts with 2-ethylmercapto-6-oxypyrimidine,⁴ in presence of alkali, giving 1-methyl-2-ethylmercapto-6-oxypyrimidine, V. They did not observe the formation of the isomeric 2-ethylmercapto-3-methyl-6-oxypyrimidine, VI. Wheeler and Liddle⁵ observed, on the other hand, that ethyl chloracetate reacts with this mercaptopyrimidine, giving 2-ethylmercapto-3-ethylacetate-6-

¹ Steudel: Z. physiol. Chem., **30**, 539.

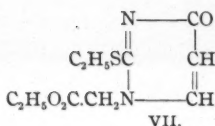
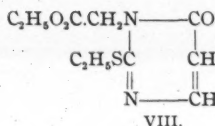
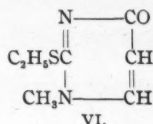
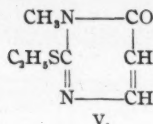
² Johnson and Heyl: THIS JOURNAL, **37**, 628; Johnson and Clapp: J. Biol. Chem. **5**, 49.

³ Loc. cit.

⁴ THIS JOURNAL, **29**, 478, 492.

⁵ J. Am. Chem. Soc., **30**, 1152.

oxypyrimidine, VII., instead of the isomeric mercaptopyrimidine, VIII.



We now find that benzyl chloride reacts with 2-ethylmercapto-6-oxypyrimidine in presence of alkali, giving a mixture of two isomeric mercaptopyrimidines melting at 77° and 139° . They were converted quantitatively into the corresponding benzyluracils melting at 175° and 173° , respectively, by hydrolysis with hydrochloric acid.

The structures of the benzyluracils and incidentally of the mercaptopyrimidines were established in the following manner: The benzyluracil melting at 173° reacted with methyl iodide, giving 1-methyl-3-benzyluracil, XVI. This same pyrimidine was also obtained by the action of benzyl chloride on 1-methyluracil,¹ XVIII. This benzyl derivative is therefore to be represented as 3-benzyluracil, XIII., and the isomer, melting at 175° , as 1-benzyluracil, XII. The mercaptopyrimidines, melting at 77° and 139° , are therefore to be assigned the structural formulas IX. and X., viz., 1-benzyl-2-ethylmercapto-6-oxypyrimidine and 2-ethylmercapto-3-benzyl-6-oxypyrimidine, since they are converted into 1-benzyluracil, XII., and 3-benzyluracil, XIII., respectively, by hydrolysis with acids.

2-Ethylmercapto-5-brom-6-oxypyrimidine² reacted with benzyl chloride, giving an excellent yield of 2-ethylmercapto-3-benzyl-5-brom-6-oxypyrimidine, XI. This was converted

¹ Johnson and Heyl: *Loc. cit.*

² *This JOURNAL*, **31**, 603.

quantitatively into 3-benzyl-5-bromuracil, XIV., by hydrolysis with hydrochloric acid. The same pyrimidine was also formed by the action of bromine on 3-benzyluracil, XIII. 1-Methyl-3-benzyl-5-bromuracil, XVII., was formed by treatment of 3-benzyl-5-bromuracil, XIV., with methyl iodide, in presence of alkali, and also by the action of bromine on 1-methyl-3-benzyluracil, XVI.

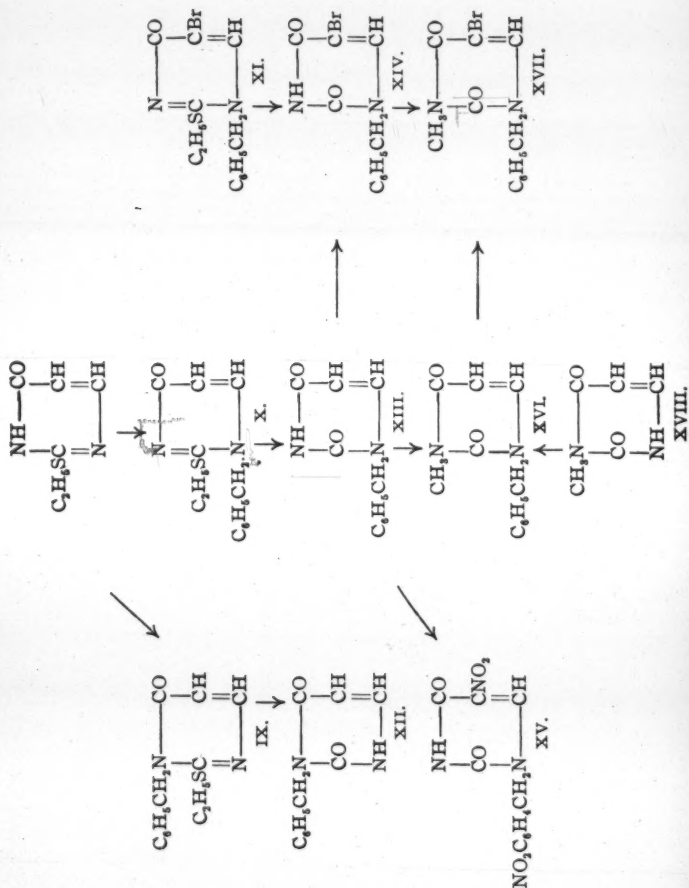
3-Benzyluracil, XIII., reacted with cold, fuming nitric acid, giving a dinitropyrimidine which we have provisionally represented as 3-*p*-nitrobenzyl-5-nitrouracil, XV.

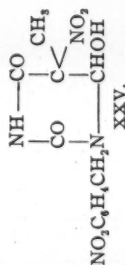
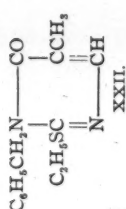
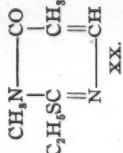
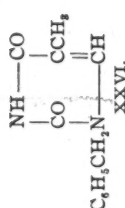
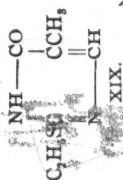
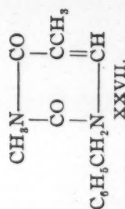
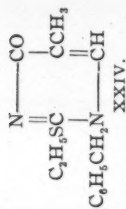
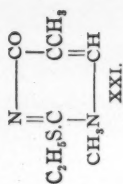
Johnson and Clapp¹ observed that 2-ethylmercapto-5-methyl-6-oxypyrimidine, XIX., reacted with methyl iodide, in presence of alkali, giving about equal proportions of 1,5-dimethyl-2-ethylmercapto-6-oxypyrimidine, XX., and 2-ethylmercapto-3,5-dimethyl-6-oxypyrimidine, XXI. We now find that benzyl chloride reacts with this mercaptopyrimidine, under the same conditions, giving 1-benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine, XXII., melting at 72°, and 2-ethylmercapto-3-benzyl-5-methyl-6-oxypyrimidine, XXIV., melting at 121°-122°. These pyrimidines were converted quantitatively into 1-benzylthymine, XXIII., melting at 205°, and 3-benzylthymine, XXVI., melting at 159°-160°, by hydrolysis with concentrated hydrochloric acid.

The structures of these four pyrimidines was determined by the behavior of the two benzylthymine towards diazobenzene-sulphonic acid. Johnson and Clapp² have shown in a recent paper that this reagent can be used to distinguish between 1- and 3-alkyl derivatives of uracil and thymine. They observed, for example, that 1-alkyl derivatives of these pyrimidines reacted with this reagent, giving red colored solutions. The isomeric 3-alkylpyrimidines, on the other hand, did not react with the diazo acid with the formation of red colors. We now find that the benzylthymine, melting at 205°, reacts with the sulphonic acid, giving a brilliant red solution, indicating that it is a 1-benzylthymine as represented by formula XXIII. The isomer gave no color with the sulphonic acid and therefore

¹ *Loc. cit.*

² *J. Biol. Chem.*, Vol. 5.





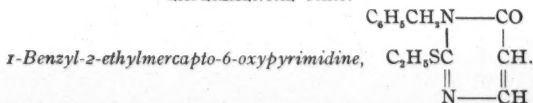
is to be assigned formula XXVI. The corresponding mercaptopyrimidines melting at 72° and 121° – 122° must therefore be represented by formulas XXII. and XXIV., respectively.

It is of interest to note here that the structures of the above benzyluracils, XII. and XIII., can also be determined by means of the diazo reagent. 1-Benzyluracil, XII., reacted with the acid, in presence of sodium hydroxide, giving a permanent red color, while its isomer, XIII., did not give a red color under the same conditions.

1-Methyl-3-benzylthymine, XXVII., was formed by the action of methyl iodide on 3-benzylthymine, XXVI. When the latter pyrimidine, XXVI., was dissolved in cold, fuming nitric acid of density 1.5 it was converted into a hydropyrimidine,¹ XXV., viz., 3-*p*-nitrobenzyloxynitrohydrothymine.

The four pyrimidines, 1-benzyluracil, 3-benzyluracil, 1-benzylthymine, and 3-benzylthymine, are characterized by their insolubility in cold water. 3-Benzyluracil and 3-benzylthymine are less soluble in water than uracil and thymine. They all crystallize from hot water without water of crystallization. They are weak acids and can be heated above their melting points without decomposition.

EXPERIMENTAL PART.



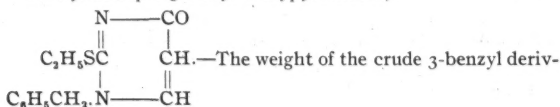
—Fifteen grams of 2-ethylmercapto-6-oxy pyrimidine and 5.4 grams of finely pulverized potassium hydroxide were dissolved in about 75 cc. of boiling absolute alcohol. Twelve and two-tenths grams of benzyl chloride were then added and the solution heated on the steam bath until it gave no alkaline reaction with moist turmeric paper (about 4 hours). After cooling, the undissolved potassium chloride was filtered off and the alcohol removed by evaporation on the steam bath. We obtained a crystalline product which was triturated with 50 cc. of a 5 per cent solution of sodium hydroxide to remove un-

¹ Johnson: THIS JOURNAL, 40, 19; J. Biol. Chem., 4, 407.

altered pyrimidine and potassium chloride. When the alkaline solution was acidified with acetic acid we recovered 1.7 grams of 2-ethylmercapto-6-oxypyrimidine. The crystalline material, insoluble in sodium hydroxide, was then extracted thoroughly with an excess of ether and the insoluble material saved (see 3-benzyl derivative below). When the ether solution was allowed to evaporate we obtained some oil and about 3.0 grams of crystalline material which melted at 65°-70° to a clear oil with no effervescence. The oil gradually assumed a crystalline form on standing. The pyrimidine separated from alcohol in well-developed prisms melting at 77°. The weight of one crystal, which was selected for analysis, was 0.3+ gram. Analysis (Kjeldahl):

N	Calculated for	Found.
	$C_{12}H_{14}ON_2S$.	
	11.38	11.63

2-Ethylmercapto-3-benzyl-6-oxypyrimidine,

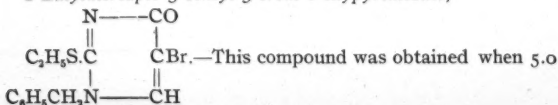


ative, insoluble in ether, in the above experiment, was 11.1 grams, corresponding to 51 per cent of the calculated. The pyrimidine is soluble in warm benzene, acetone, alcohol, very soluble in chloroform, and practically insoluble in cold ether and ligroin. It is difficultly soluble in hot water and crystallizes in long, slender prisms, and hexagonal prisms or flat tables melting at 139° to an oil. This melting point was not raised by recrystallization from benzene.

Analysis (Kjeldahl):

N	Calculated for	Found.	
	$C_{12}H_{14}ON_2S$.	I.	II.
	11.38	11.58	11.61

2-Ethylmercapto-3-benzyl-5-brom-6-oxypyrimidine,



grams of 2-ethylmercapto-5-brom-6-oxypyrimidine¹ were heated in absolute alcohol, for 4 to 5 hours, with the required proportions of potassium hydroxide and benzyl chloride. After filtration from the undissolved potassium chloride and evaporation of the alcohol we obtained a semisolid substance which immediately solidified when washed with ether. The yield was 4.2 grams, corresponding to 60.0 per cent of the calculated. The pyrimidine is difficultly soluble in water and separates from a hot, aqueous solution in needles melting at 129° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{13}ON_2BrS$.	Found.
N	8.62	9.0
<i>1-Benzyluracil</i> ,	$ \begin{array}{c} C_6H_5CH_2N \text{---} CO \\ \qquad \qquad \\ CO \qquad \qquad CH \text{---} A \text{ quantitative yield} \\ \qquad \qquad \\ NH \text{---} CH \end{array} $	

of this pyrimidine was obtained when 3.0 grams of the corresponding 2-mercaptopyrimidine were dissolved in 150 cc. of concentrated hydrochloric acid and the solution evaporated to dryness. It crystallizes from hot water in prismatic crystals melting at 175° to a clear oil. It did not contain water of crystallization. When mixed with the isomeric 3-benzyluracil (see below) melting at 173°, the fusion point was lowered to 140°-155°. The pyrimidine reacted with diazobenzenesulphonic acid, in presence of alkali, giving a red colored solution. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}O_2N_2$.	Found.
N	13.86	14.1
<i>3-Benzyluracil</i> ,	$ \begin{array}{c} NH \text{---} CO \\ \qquad \qquad \\ CO \qquad \qquad CH \text{---} This \text{ pyrimidine was} \\ \qquad \qquad \\ C_6H_5CH_2N \text{---} CH \end{array} $	

prepared by digesting 6.7 grams of 2-ethylmercapto-3-benzyl-6-oxypyrimidine with concentrated hydrochloric acid for 5 to 6

¹ Wheeler and Johnson: *THIS JOURNAL*, **31**, 603.

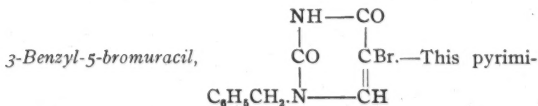
hours. The yield was 5.5 grams or 96 per cent of the theoretical. It crystallizes from alcohol in stout prisms melting at 173° to a clear oil with no effervescence. It is difficultly soluble in water and moderately soluble in cold acetone; insoluble in cold benzene and ether; and difficultly soluble in chloroform. It was insoluble in cold 25 per cent hydrochloric and sulphuric acids and easily soluble in warm glacial acetic acid. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}O_2N_2$.	I.	Found.	II.
N	13.86	13.9		14.0

This pyrimidine does not react with diazobenzenesulphonic acid to give a red colored solution. The mixture assumed a yellow color, which was permanent for 30 minutes.

Solubility of 3-Benzyluracil in Water.—One hundred parts of water dissolved at 25°

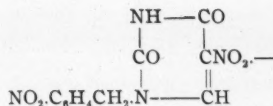
I.	II.
0.0998 gram.	0.1008 gram.



dine can be prepared by treating 3-benzyluracil in glacial acetic acid with the calculated quantity of bromine. It crystallizes from acetic acid in hexagonal prisms melting at 204° to a clear oil. The same brompyrimidine was also prepared by dissolving 0.5 gram of 3-benzyluracil in bromine water and allowing the solution to evaporate to dryness. The residue, about 0.8–0.9 gram, was then digested with absolute alcohol for 2 hours and the solution evaporated to dryness. The compound obtained by this treatment crystallized from alcohol in prisms melting at 204° . A quantitative yield of the pyrimidine was also obtained by digesting 2-ethylmercapto-3-benzyl-5-brom-6-oxypyrimidine with concentrated hydrochloric acid. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}O_2N_2\text{Br}$.	Found.
N	9.96	10.0

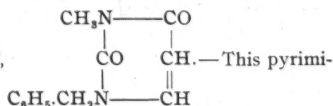
3-p-Nitrobenzyl-5-nitouracil,



Five-tenths of a gram of 3-benzyluracil was dissolved, at ordinary temperature, in 10 cc. of fuming nitric acid of density 1.5. The acid solution was then allowed to stand at ordinary temperature when prismatic crystals separated. They were purified for analysis by recrystallization from hot water. The pyrimidine is difficultly soluble and separates in slender prisms, which decompose, according to the rate of heating, at 235°–240° with effervescence. Analysis (Kjeldahl):

	Calculated for $\text{C}_{11}\text{H}_8\text{O}_4\text{N}_4$	Calculated for $\text{C}_{11}\text{H}_8\text{O}_4\text{N}_4$	I. Found.	II.
N	19.18	17.00	19.48	19.39

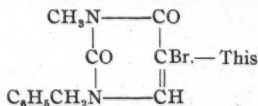
1-Methyl-3-benzyluracil,



dine is easily prepared by dissolving 3-benzyluracil and one molecular proportion of potassium hydroxide in alcohol and then warming with an excess of methyl iodide. The same pyrimidine was also obtained when 1-methyluracil¹ was digested in alcohol with the calculated proportions of potassium hydroxide and benzyl chloride. The pyrimidine is extremely soluble in alcohol and benzene. It crystallizes from dilute alcohol in needles melting at 75° to an oil without effervescence. Analysis (Kjeldahl):

	Calculated for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_3$	I. Found.	II.
N	12.96	13.17	13.12

1-Methyl-3-benzyl-5-bromuracil,



pyrimidine was prepared in two ways:

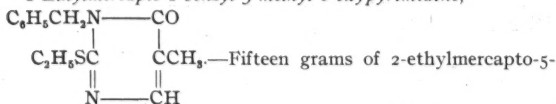
¹ Johnson and Heyl: *Loc. cit.*

1. By dissolving 1-methyl-3-benzyluracil in glacial acetic acid and then adding the calculated amount of bromine. They reacted with evolution of heat. The pyrimidine was very soluble in glacial acetic acid but was precipitated by diluting with water.

2. By warming 0.8 gram of 3-benzyl-5-bromuracil in methyl alcohol with 1.9 grams of methyl iodide and 0.1 gram of metallic sodium. The alkylation was very smooth and the solution was neutral in a few minutes. The pyrimidine crystallizes from alcohol in diamond-shaped prisms melting at 123° to a clear oil with no effervescence. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{11}O_2N_2Br$.	Found.
N	9.50	9.8

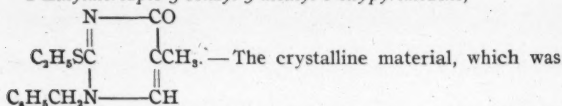
2-Ethylmercapto-1-benzyl-5-methyl-6-oxypyrimidine,



methyl-6-oxypyrimidine and 4.9 grams of finely pulverized potassium hydroxide were dissolved in 75 cc. of absolute alcohol. Eleven and two-tenths grams of benzyl chloride were then added and the solution heated on the steam bath for 6 hours. After filtering from undissolved potassium chloride and evaporation of the alcohol we obtained a crystalline product which was washed with 50 cc. of a 5 per cent solution of sodium hydroxide. Four and four-tenths grams of unaltered pyrimidine deposited when the sodium hydroxide solution was acidified with acetic acid. The crystalline material, insoluble in sodium hydroxide, was then extracted in the usual manner with ether and the insoluble portion saved (see 3-benzyl derivative below). From the ether washings we obtained about 3.0 grams of pyrimidine melting at 65° – 66° . The compound is very soluble in acetone, benzene, and ether. It separates from dilute alcohol in stout prisms melting at 70° to a clear oil without effervescence. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{13}ON_2S$.	Found.
N	10.77	10.9

2-Ethylmercapto-3-benzyl-5-methyl-6-oxypyrimidine,



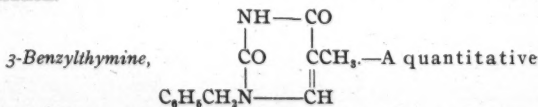
—The crystalline material, which was insoluble in ether, in the above experiment represented this pyrimidine and weighed 11.2 grams, corresponding to 68 per cent of the calculated. The pyrimidine is extremely soluble in alcohol and acetone. It was purified for analysis by recrystallization from benzene. It separated in hexagonal plates melting at 121°–122°. Analysis (Kjeldahl):

N	Calculated for	Found.
	$\text{C}_{14}\text{H}_{16}\text{ON}_2\text{S}$	
	10.77	11.1
	$ \begin{array}{c} \text{C}_6\text{H}_5\text{CH}_2\text{N} \text{---} \text{CO} \\ \parallel \qquad \parallel \\ \text{CO} \qquad \text{CCH}_3 \\ \parallel \qquad \parallel \\ \text{NH} \text{---} \text{CH} \end{array} $	
1-Benzylthymine,	—One and eight-	

tenths grams of 1-benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine were digested with concentrated hydrochloric acid until the evolution of ethyl mercaptan ceased. When this solution was evaporated to dryness the benzylthymine was obtained as a crystalline compound. The pyrimidine separated from hot alcohol in clusters of radiating prisms which melted at 204°–205° to a clear oil. The pyrimidine is difficultly soluble in water. Analysis (Kjeldahl):

N	Calculated for	Found.
	$\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}_2$	
	12.96	13.3

This compound reacted with diazobenzenesulphonic acid, in presence of sodium hydroxide, giving a beautiful, claret red solution.



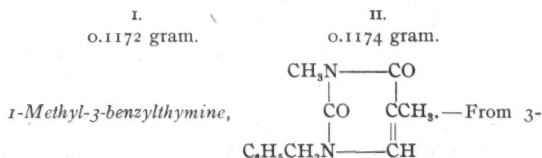
3-Benzylthymine, —A quantitative yield of this pyrimidine was obtained when the corresponding

2-mercaptopyrimidine was digested with concentrated hydrochloric acid until the evolution of ethyl mercaptan ceased. The pyrimidine is easily soluble in alcohol, acetone, benzene, and difficultly soluble in ether. It is very soluble in glacial acetic acid and chloroform and difficultly soluble in cold 25 per cent hydrochloric and sulphuric acids. It separates from hot water in diamond-shaped prisms melting at 160° to a clear oil with no effervescence. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}O_2N_2$	Found.
N	12.96	13.2

This pyrimidine did not react with diazobenzenesulphonic acid to give a red color. The mixture assumed a yellow color which remained permanent for over one hour.

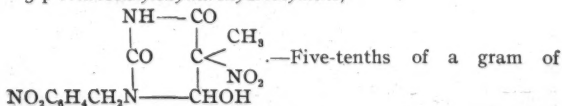
Solubility of 3-Benzylthymine in Water.—One hundred parts of water dissolved at 25°



benzylthymine and methyl iodide. It crystallized from water in prismatic crystals melting at 101° to a clear oil. It did not react with diazobenzenesulphonic acid to give a red color. Analysis (Kjeldahl):

	Calculated for $C_{13}H_{14}O_2N_2$	Found.
N	12.17	12.07

3-p-Nitrobenzylthymine,



3-benzylthymine was dissolved in 10 cc. of cold fuming nitric acid of density 1.5. There was only slight evolution of heat

and the pyrimidine dissolved to a clear, yellow solution. On standing exposed to the atmosphere well-developed prisms separated. They decomposed at 176° with violent effervescence. A nitrogen determination indicated that a nitro group had entered the benzene ring and that nitric acid had added to the double bond in the 4,5 positions of the pyrimidine ring. Analysis (Kjeldahl):

	Calculated for			Found.
	$C_{12}H_{12}O_7N_4$	$C_{12}H_{12}O_8N_3$	$C_{12}H_{11}O_8N_3$	
N	17.28	14.33	16.0	17.11

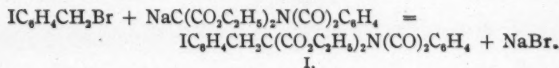
NEW HAVEN, CONN.,
June, 1908.

CLXII.—RESEARCHES ON HALOGEN AMINO ACIDS: PARAIODPHENYLALANINE.

[FIFTH PAPER.]

BY HENRY L. WHEELER AND SAMUEL H. CLAPP.

Our work on the halogen substitution products of phenylalanine has now been extended so as to include *p*-iodphenylalanine. The starting point for the preparation of this acid was *p*-iodtoluene, melting at 35° – 36° . This was converted into *p*-iodbenzyl bromide as described by Jackson.¹ When this reactive halide was heated with the sodium salt of phthalimidomalonic ester, in the manner described by Sørensen² in his synthesis of phenylalanine, an almost quantitative reaction took place as follows:

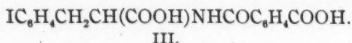
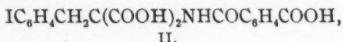


When *p*-iodbenzylphthalimidomalonic ester, I., thus formed, was warmed with alkali and the solution acidified with hydrochloric acid while warm, carbon dioxide was evolved and the phthalamic acid, III., separated. If the solution was acidi-

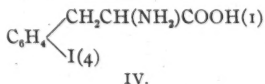
¹ THIS JOURNAL, 1, 103 (1879).

² Compt. rend. Trav. Lab. Carlsberg, 8, 6 (1902); Centrabl., 1903, II., 33; Z. physiol. Chem., 44, 448 (1905).

fied while cold, a mixture of the two phthalamic acids, II. and III., was obtained.



Even a moderate treatment of the phthalamic acids with hot hydrochloric acid was sufficient to effect hydrolysis of the acid amide group, and on evaporating a mixture of phthalic acid and *p*-iodophenylalanine hydrochloride was obtained. Phthalic acid was dissolved and the free *p*-iodophenylalanine, IV., was obtained by dissolving the mixture in ammonia and then evaporating or precipitating with acetic acid.



p-Iodophenylalanine and the intermediate compounds in the present synthesis immediately liberate iodine when treated with concentrated sulphuric acid. Iodine vapors fill the flask in the Kjeldahl analyses. The substances are far more stable towards concentrated hydrochloric acid. No iodine was removed by this acid when the solutions were digested on the steam bath for a few hours. Iodine was not removed in the above synthesis if the treatment with alkali was not too energetic. If the alcoholic solution of phthalimidomalonate ester was warmed too long with alkali, iodine could then be detected by treating the solution with dilute sulphuric acid and potassium nitrite and then shaking with chloroform.

It is noteworthy that *p*-iodophenylalanine or its silver salt can be boiled with an aqueous solution of silver nitrate and nitric acid without separating silver iodide. On the other hand iodogorgoic acid or diiodotyrosine readily gives up all of the iodine as silver iodide by this treatment.¹ The

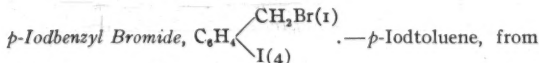
¹ Wheeler and Jamieson: *THIS JOURNAL*, **33**, 365 (1905).

separation of silver iodide in the case of diiodtyrosine is quite characteristic. The clear solution on warming suddenly becomes turbid just as the boiling point is reached and the yellow solid causing the turbidity soon after separates as a heavy precipitate with the characteristic appearance of silver iodide.

Since diiodtyrosine contains 58.6 per cent of iodine this reaction serves as a delicate test for the acid.

It is now interesting to note that when sponges are boiled with barium hydroxide a solution containing an iodamino acid is obtained which separates silver iodide in precisely the same manner as described above when heated with a solution of silver nitrate and nitric acid.

EXPERIMENTAL PART.



Kahlbaum, was distilled at about 25 mm. pressure. It boiled at 113° and solidified to a light yellowish, crystalline mass melting at $35^\circ\text{--}36^\circ$. This was converted into *p*-iodbenzyl bromide¹ as follows: Twenty grams of bromine were added in small drops to 25.8 grams of *p*-iodtoluene heated in an oil bath. The temperature of the bath at first was 180° , then it was kept at 170° . About 15 minutes was taken to add the bromine. On cooling, the contents of the flask solidified to a dark colored, crystalline mass. This was treated with small quantities of cold alcohol, which removed the color, and on filtering and washing thoroughly with cold alcohol 17.7 grams of *p*-iodbenzyl bromide, melting at $75^\circ\text{--}78^\circ$, were obtained. From the alcoholic washings, on evaporating at ordinary temperature, 1.6 grams more of the bromide were obtained. This made the yield 54.8 per cent of the calculated. The remaining material was a dark colored oil which did not solidify after standing a long time in the open air.

In another experiment 55.3 grams of *p*-iodtoluene and 41.0 grams of bromine at $140^\circ\text{--}145^\circ$, taking about one-half hour

¹ Jackson: *Loc. cit.* See also Jackson and Mabery: *THIS JOURNAL*, 2, 250 (1880).

to add the bromine, gave 34.7 grams of *p*-iodbenzyl bromide. This yield is 46 per cent of the calculated.

p-Iodobenzylphthalimidomalonic Ester,

$\text{IC}_6\text{H}_4\text{CH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2\text{N}(\text{CO})_2\text{C}_6\text{H}_4$.—Seventeen grams of *p*-iodbenzyl bromide were added to the dry sodium salt of phthalimidomalonic ester, prepared according to Sørensen's directions from 17.4 grams of phthalimidomalonic ester and 1.3 grams of sodium. The mixture was heated for several hours in an oil bath at 130° – 140° . It reacted slowly, the yellow color became lighter, and the mass liquefied. The temperature of the bath was then maintained at 150° – 160° until the original yellow color disappeared. The flask was then cooled and the contents extracted with 100 cc. of hot water. The undissolved material was crystallized from alcohol. Beautiful, flat, colorless prisms or six-sided plates separated. They melted at 112° to a clear oil. The yield was 24.5 grams or 85.8 per cent of the calculated.

I. 0.1251 gram substance required 2.5 cc. 0.1 N HCl.

II. 0.3215 gram substance required 6.1 cc. 0.1 N HCl.

III. 0.2024 gram substance gave 0.0911 gram AgI.

IV. 0.1290 gram substance gave 0.0594 gram AgI.

	Calculated for $\text{C}_{23}\text{H}_{20}\text{O}_6\text{NI}$.	I.	II.	Found.	III.	IV.
N	2.68	2.79	2.65	...	...	...
I	24.38	...	...	...	24.32	24.87

p-Iodobenzylphthalimidomalonic ester is insoluble in water but readily soluble in hot alcohol. Concentrated sulphuric acid immediately liberates iodine. Toward hydrochloric acid the ester is far more stable. Two grams of the ester were dissolved in 100 cc. of 95 per cent alcohol and 25 cc. of concentrated hydrochloric acid were added. The solution was boiled under a return condenser for several hours. It was then evaporated to dryness and the oily residue was crystallized from alcohol. Six-sided plates, which melted at 112° and therefore were unaltered material, separated. There was no evidence of iodine being displaced.

When this ester is warmed with dilute alkali or barium

hydroxide it is readily saponified and it was found that the solutions could be boiled for a moderate length of time without giving a test for iodine when treated with sodium nitrite, acidified with sulphuric acid, and shaken with chloroform.

Sixteen grams of the ester, dissolved in a small amount of boiling alcohol, and 6.9 grams of potassium hydroxide in 400 cc. of water gave no test for iodine as above when warmed on the steam bath for 10 minutes, although the ester was saponified.

When the same quantities were warmed a half hour a faint test for iodine was obtained.

p-Iodobenzylaceticphthalamic Acid,

$\text{IC}_6\text{H}_4\text{CH}_2\text{CH}(\text{COOH})\text{NHCOC}_6\text{H}_4\text{COOH}$.—Seven and one-half grams of the above ester were dissolved in alcohol and 5 grams of potassium hydroxide in a little water were added to the hot solution. The solution was warmed for an hour on the steam bath, the alcohol evaporated, and the residue taken up in water and acidified with hydrochloric acid. The precipitate thus obtained, melting at 178° , weighed 6.3 grams, which corresponds with the calculated. The solution, however, gave a test for iodine.

When the material is precipitated from hot alkaline solutions by means of hydrochloric acid it separates in the form of fine looking needles melting at 178° – 179° , otherwise it separates in a doughy or stringy condition.

In one experiment ten grams of *p*-iodobenzylphthalimidomalononic ester were dissolved in 50 cc. of 95 per cent alcohol and to the hot solution 4.0 grams of sodium hydroxide in 30 cc. of water were added. Three grams sodium hydroxide is the calculated amount for 4 molecules. The solution remained clear immediately after the addition of the alkali but in a few minutes a heavy mass of crystals of the sodium salt separated. It is evident from this that the saponification takes place with alkali with ease.

The flask was left on the steam bath a few minutes after the sodium salt had separated, whereupon the solution suddenly bumped so violently that almost half the material was lost. The alkaline solution gave no color test for iodine with

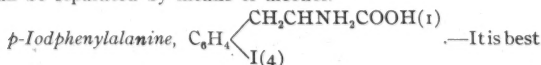
sodium nitrite and sulphuric acid. When precipitated with hydrochloric acid, after evaporating the alcohol, and warmed, the doughy mass first obtained was seen to be full of bubbles (carbon dioxide). Some of this precipitate dissolved and then in a few minutes needles separated from the warm solution and the undissolved material changed to a granular powder. Both the needles and the powder melted with effervescence at 179° . This material is practically insoluble in water, but very soluble in alcohol.

Analyses of the needles:

- I. 0.2625 gram substance required 6.1 cc. 0.1 N HCl.
 II. 0.2200 gram substance required 5.0 cc. 0.1 N HCl.

	Calculated for $C_{17}H_{14}O_4NI$.	I.	Found.	II.
N	3.19	3.25		3.18

The saponification with alkali does not usually stop precisely at this phthalamic acid, a portion of the material being further hydrolyzed to *p*-iodphenylalanine. The compounds can be separated by means of alcohol.



to saponify the *p*-iodbenzylphthalimidomalonic ester with potassium hydroxide. The solution is less liable to bump. The precipitate produced, after evaporation of the alcohol, by the addition of hydrochloric acid was digested with 20 per cent hydrochloric acid for about two hours on the steam bath. No iodine appeared to be liberated in this treatment. On concentrating to a small volume and adding concentrated hydrochloric acid the amino acid can be precipitated as the hydrochloride. The precipitate, however, contains phthalic acid. It was found best to evaporate to dryness, then treat the residue with a little water, and evaporate again to dryness. The residue was dissolved in ammonia and the *p*-iodphenylalanine either precipitated by acetic acid (Analysis III. The yield was almost quantitative), or the ammonia solution was evaporated on the steam bath. For example,

1.5 grams of the acid were dissolved in strong ammonia and the ammonia evaporated. Clusters of thin scales, which weighed 1.1 grams, separated when the solution had no odor of ammonia (Analysis II.). The filtrate deposited another crop of plates on further evaporation, and it gave a test for iodine with potassium nitrite and sulphuric acid.

If the hydrochloric acid solution is evaporated to dryness, taken up in water, the operation repeated, and the residue then boiled with water and alcohol, the hydrochloric acid salt dissociates and free *p*-iodophenylalanine remains undissolved. (Analysis I.).

I. 0.2434 gram substance required 8.4 cc. 0.1 N HCl.

II. 0.2460 gram substance required 8.7 cc. 0.1 N HCl.

III. 0.1394 gram substance gave 0.1119 gram AgI (Carius).

	Calculated for $C_9H_{10}O_2NI$	I.	Found. II.	III.
N	4.81	4.83	4.95	...
I	43.64	...	...	43.38

p-Iodophenylalanine is very slightly soluble in water even at 100°. It is also very sparingly soluble in alcohol. It is readily dissolved by hot acetic acid and this is the best solvent from which to crystallize the substance. It forms thin scales with an irregular outline and the resemblance to phenylalanine is very striking. It melts to an oil with vigorous effervescence at 270°. The melting point may vary a few degrees according to the rate of heating.

A solution of the acid in 20 per cent sulphuric acid is partially precipitated by a strong solution of phosphotungstic acid in 5 per cent sulphuric acid. The precipitate dissolves on warming and does not form if acetic acid is present. The ammonia solution of the acid gave no precipitate with barium chloride. About 0.2 gram of the acid was dissolved in 100 cc. of a solution of barium hydroxide, saturated at ordinary temperature, and this solution was allowed to digest on the steam bath for about a week. It was then filtered from some barium carbonate and acidified with nitric acid. On adding silver nitrate no silver iodide was precipitated.

Action of Sodium Hydroxide.—One-tenth gram of *p*-iodophenylalanine was boiled for a few minutes in an open flask with about 5 cc. of 33 per cent sodium hydroxide. On cooling, a crystalline sodium salt separated, difficultly soluble in sodium hydroxide and very readily soluble in water. Under these conditions no iodine could be detected in this solution with nitrous acid.

In a second experiment about 0.2 gram of *p*-iodophenylalanine was warmed on the water bath with 20 cc. of 33 per cent sodium hydroxide for five and a half hours. The solution then gave a pronounced test for iodine with nitrous acid and a very weak Millon's reaction. The solution was warmed for 5 hours longer on the water bath, made weakly acid with hydrochloric acid, and then weakly alkaline with ammonia. After filtering from inorganic material the solution was concentrated. About 0.1 gram of substance, practically insoluble in boiling water, which contained iodine and was therefore unaltered *p*-iodophenylalanine, separated out.

The hydrochloride, $\text{IC}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2\text{HCl})\text{COOH}$, was prepared by dissolving *p*-iodophenylalanine in hot dilute hydrochloric acid and then adding concentrated hydrochloric acid. It separated in clusters of very thin, flat, colorless plates with irregular outlines. It is very insoluble in strong hydrochloric acid and it is dissociated by boiling water. It was dried over sulphuric acid and potassium hydroxide.

0.0985 gram substance gave 0.0424 gram AgCl.

	Calculated for $\text{C}_9\text{H}_{10}\text{O}_2\text{NI}\cdot\text{HCl}$.	Found.
Cl	10.84	10.64

This salt decomposed at about 248° when not too slowly heated.

The silver salt was prepared by adding an aqueous solution of silver nitrate to a neutral solution of the acid in ammonia, or to a solution of the acid in 0.1 N potassium hydroxide. It forms a white, nongelatinous precipitate which is readily soluble in ammonia or dilute nitric acid. It differs decidedly from the silver salt of diiodtyrosine inasmuch as the nitric

acid solution can be boiled for some time without the separation of silver iodide.

The Copper Salt, $(\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{COO})_2\text{Cu}$.—*p*-Iodophenylalanine dissolved in the calculated quantity of 0.1 N sodium hydroxide gave a light blue, gelatinous precipitate with copper sulphate. When boiled with water it became more granular but it showed no characteristic crystalline form. When dried in the air it formed a light blue powder. It was almost insoluble in boiling water and alcohol and it did not lose weight at $85^\circ\text{--}90^\circ$.

0.1693 gram substance gave 0.0214 gram CuO.

	Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_4\text{N}_2\text{I}_2\text{Cu}$.	Found.
Cu	9.88	10.10

The phenylisocyanate derivative was prepared by dissolving *p*-iodophenylalanine in the calculated quantity of 0.1 N sodium hydroxide and then adding a slight excess of phenyl isocyanate. Some heat was evolved and a crystalline mass of diphenylurea and the sodium salt of the hydantoic acid separated. Water was added and the solution, on filtering and acidifying with hydrochloric acid, deposited the hydantoic acid as an oil which solidified to a crystalline mass. The substance is insoluble in water and petroleum ether. It is readily soluble in alcohol and very soluble in ether. It crystallizes from alcohol in aggregates of flat prisms or plates, best on adding a little water. It melts at $178^\circ\text{--}179^\circ$ with brisk effervescence.

0.1656 gram substance required 8.0 cc. 0.1 N HCl.

	Calculated for $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}_2\text{I}$ (hydantoin).	Calculated for $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2\text{I}$.	Found.
N	7.14	6.83	6.76

The hydantoin was prepared by boiling the above phenyl isocyanate derivative with 20 per cent hydrochloric acid for 3 hours. The hydrochloric acid was then evaporated and the material was crystallized from alcohol. It was found to be much less soluble in alcohol than the hydantoic acid and

it formed large, flat, rhombohedral crystals. It melted to a clear oil without effervescence at 195° – 196° .

0.1069 gram of substance required 5.7 cc. 0.1 N HCl.

N	Calculated for	Found.
	$C_{16}H_{15}O_2N_2I$.	
	7.14	7.46

p-Iodophenylalanine Ethyl Ester, $IC_6H_4CH_2CH(NH_2)COOC_2H_5$.—Three and seven-tenths grams of *p*-iodophenylalanine were suspended in 200 cc. of absolute alcohol and a rapid stream of dry hydrogen chloride was passed through the solution without cooling; the precipitate went rapidly into solution. The solution was then evaporated to dryness under diminished pressure. The crystalline residue was suspended in 200 cc. of absolute alcohol and the operation repeated. The residue was dissolved in ice water, ether was added, the solution containing the hydrochloride was neutralized with 33 per cent sodium hydroxide, and the free ester at once removed in the ether. The ether solution was shaken 15 minutes with anhydrous potassium carbonate, and dried for two days over anhydrous sodium sulphate. The ether was then evaporated on the water bath and a thick oil was obtained, from which, when cooled, a small amount of gelatinous solid separated. This went into solution again on warming. The whole was distilled at about 25 mm. pressure, whereupon the oil practically all boiled at 223° – 226° . The weight of distilled ester was 2 grams or 50 per cent of the calculated. During the distillation no evidence of decomposition was observed. A very small amount of crystalline residue remained in the distilling bulb.

The *p*-iodophenylalanine ethyl ester formed a thick, colorless oil difficultly soluble in water, which was converted into the picrate for analysis.

The Picrate, $IC_6H_4CH_2CH(NH_2)COOC_2H_5 \cdot C_6H_3O_7N_3$.—The distilled oil was dissolved in alcohol and an aqueous solution of picric acid in excess was added. The yellow precipitate was recrystallized from alcohol. It then formed flat plates

or tables which melted to a clear red oil, without conspicuous effervescence, at 200°–203°.

0.1250 gram substance required 9.3 cc. 0.1 N HCl.

	Calculated for $C_{11}H_{14}O_2NL.C_6H_5O_7N_3$.	Found.
N	10.22	10.42
NEW HAVEN, CONN., June, 1908.		

A STUDY OF THE REFRACTIVE INDICES OF SOME SOLUTIONS.

BY FREDERICK H. GETMAN AND F. B. WILSON.

In their recent work on hydration in solution; Jones and Getman¹ measured the refractive indices of the solutions studied in order to determine whether there was any minimum in the refractivity-concentration curves similar to that found in the freezing point-concentration diagrams. In every case the refractive index was found to be a linear function of the concentration. From this the authors concluded that the measurement of the refractive index of a solution does not enable one to determine whether hydration has taken place or not. If combination between solute and solvent does occur, or if owing to the attraction of the solute some of the solvent is removed from the rôle of purely solvent action, then we should expect some change in the refractive power of the solution.

With a view to further testing this point the present investigation was undertaken.

Instead of following the change in refractive index with change in concentration of the solution, we have compared specific refractions with corresponding concentrations. The relation of specific refraction, R , to refractive index is given by the empirical formula of Gladstone and Dale,²

$$\frac{n-1}{d} = R,$$

¹ Z. physik. Chem., **48**, 244. Phys. Rev., **18**, 146. THIS JOURNAL, **31**, 303. Z. physik. Chem., **49**, 407. Pub. No. 60, Carnegie Institution.

² Phil. Trans., **1888**, 887.

where n is the refractive index and d is the density of the solution. Other formulae for specific refraction have been proposed, notably those of Newton, Lorenz-Lorentz, and Edwards. The Gladstone and Dale formula was selected in preference to any of the others because of its being quite independent of slight changes in temperature, as has been pointed out by Landolt.¹

The apparatus employed for the measurement of the refractive indices of the solutions was a Pulfrich refractometer made by Wolz. This form of instrument, not being furnished with any temperature regulating device, has the disadvantage that both prism and solution are subject to the same thermal variation as the air of the room. The temperature of the room remained very nearly constant throughout the work, the greatest variation being five degrees. An attempt was made to bring all of the measurements to one temperature by heating and cooling the solutions and thus working out a table of temperature coefficients for several concentrations of each solution. This proved to be impracticable since we possessed no means of determining when thermal equilibrium was finally established between prism and solution. By using the Gladstone and Dale formula, however, it is certain that no appreciable error can be traced to temperature variations. All measurements of refractive indices were made for the D line, a Bunsen flame fed with sodium chloride being the source of light.

The densities of the solutions were taken from the tables of Landolt and Börnstein and the Smithsonian Physical Tables.

All solutions were made up on the percentage basis. Some of the data recorded in this paper have been calculated from the measurements of refractive indices made by other workers. Where such material has been drawn upon, suitable acknowledgment will be made in the proper place.

If the specific refraction of a solution of definite percentage concentration is known and the specific refraction of the solvent is also determined, the specific refraction of the solute

¹ *Pogg. Ann.*, 133, 595.

may be easily calculated. In Fig. I., let O be the origin of a system of rectangular coördinates, in which abscissae denote percentage concentrations and ordinates specific refractions. Let A represent the pure solvent of specific refraction R , let B denote the solution of concentration p and specific refraction R_1 , and let C be the pure solute whose specific refraction R_2 is sought.

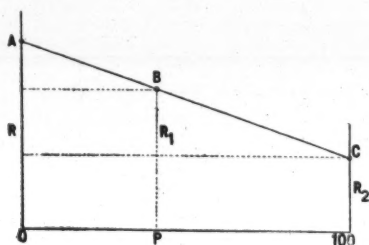


Fig. I.

From the diagram it is evident that

$$\frac{R - R_1}{p} = \frac{R - R_2}{100},$$

or

$$R_2 = R - \frac{100(R - R_1)}{p} \quad (1).$$

Substituting $(n - 1)/d$, $(n_1 - 1)/d_1$, and $(n_2 - 1)/d_2$ for R , R_1 , and R_2 respectively, in (1), we get

$$\frac{n_2 - 1}{d_2} = \frac{n_1 - 1}{d_1} \cdot \frac{100}{p} - \frac{n - 1}{d} \cdot \frac{100 - p}{p} \quad (2).$$

Equation (2) is identical with that used by Gladstone and Dale¹ for the calculation of the specific refraction of a solid from its solution.

These authors found close agreement between the specific refraction determined from the solution and that determined

¹ Phil. Trans., 1888, 887.

40
8

directly from the pure solute. Subsequent work by other investigators, notably Bedson and Williams,¹ Kanonnikow,² Nasini,³ Damien,⁴ LeBlanc,⁵ and F. Schütt,⁶ has failed to confirm the original statements of Gladstone and Dale. In some cases there is marked discrepancy between the values of specific refractivity as calculated from a solution and that determined directly from the solute. This difference appears to be greater when the solute is a salt than when it is a non-electrolyte. In explanation of this Ostwald says: "die Zustandsänderung, welche ein Salz beim Auflösen im Wasser erfährt, sehr viel tiefer gehender Natur ist, als die, welche in-differente Stoffe erleiden."⁷

Then, too, many salts form anisotropic crystals whose refractive constants are different in different directions. This may partially account for the lack of agreement between the specific refraction as calculated from the solution and as determined from the pure salt.

The specific refraction of a salt may also be calculated from the refractive equivalents of its constituent elements. Landolt⁸ has shown that the sum of the refractive equivalents of the elements which enter into a compound, divided by its molecular weight, gives the specific refraction of the compound.

Here also there is not perfect agreement between the specific refraction calculated from the refraction equivalents and that found by direct measurements of the refractive index and density of the solid substance.

The differences between the values of the specific refractions as calculated and observed for fifteen of the substances studied in this paper are given in Table I.:

¹ Ber. d. chem. Ges., 14, 2549.

² J. prakt. Chem. [2], 31, 321.

³ Accad. dei Lincei, 8, 1884.

⁴ Ann. de l'Ecole Norm. Sup. [2], 10.

⁵ Z. physik. Chem., 4, 559.

⁶ *Ibid.*, 5, 349.

⁷ "Lehrb. allg. Chem.," I., 429.

⁸ Wied. Ann., 123, 611.

Table I.

Solute.	<i>R</i> (calc.).	<i>R</i> (obs.).	Solute.	<i>R</i> (calc.).	<i>R</i> (obs.).
NaCl	0.2649	0.2426	CuSO ₄ ·5H ₂ O	0.2632	0.2318
NaNO ₃	0.2211	0.2593	CH ₃ COOH	0.3567	0.3525
KCl	0.2486	0.2459	<i>n</i> -C ₈ H ₇ COOH	0.4159	0.4122
KBr	0.2079	0.2029	CH ₃ OH	0.4062	0.4122
KI	0.2144	0.2171	C ₂ H ₅ OH	0.4478	0.4506
KNO ₃	0.2131	0.2397	C ₃ H ₇ (OH) ₃	0.3673	0.3738
K ₂ CrO ₄	0.2722	0.2666	C ₁₂ H ₂₂ O ₁₁	0.3491	0.3585
CaCl ₂ ·6H ₂ O	0.2913	0.2521			

Because of this lack of agreement between the observed and calculated values of *R* and because the indices of refraction of several of the salts studied have not been measured, it was decided to use only the values of specific refractions calculated from refractive equivalents. Further, when a salt has water of crystallization the specific refraction has been uniformly calculated for the anhydrous salt.

Before measuring the refractive indices of any solutions the refractive index of pure water was determined at several temperatures and the corresponding specific refraction calculated by means of the Gladstone and Dale formula.

Table II. shows the values of the index for water at different temperatures and also gives the specific refraction *R*, as calculated. The temperature coefficient of refraction is also tabulated, but as was pointed out above, the form of refractometer used does not admit of sufficiently accurate control of the temperature to render these coefficients trustworthy. The table also emphasizes what was said as to the Gladstone and Dale formula being quite independent of temperature changes.

Table II.—Water.

<i>t</i> .	<i>d</i> .	<i>n</i> .	<i>dn/dt</i> .	(<i>n</i> - 1)/ <i>d</i> = <i>R</i> .
15	0.99916	1.33379		0.3341
22.6	0.99769	1.33309	0.000092	0.3337
30	0.99577	1.33239	0.000094	0.3338
35	0.99418	1.33193	0.000092	0.3338
40	0.99235	1.33139	0.000108	0.3338

Mean, 0.3338

The salts used in this investigation were obtained from Kahlbaum. The solutions were made up on the percentage basis with pure distilled water, the most concentrated solution for each salt being almost saturated. Several concentrations of each solute were prepared and the refractive indices measured, and from the tables of densities the specific refractions were calculated. By means of equation (2) the specific refraction of the solute was calculated from the specific refraction of each solution, the value of the specific refraction of water being taken as 0.3338.

The measurements and the calculated data are recorded in the following tables. In these tables the notation is as follows: p = percentage concentration, d = density, n = index of refraction, R_1 and R_2 = specific refraction of solution and solute, respectively.

Table III.—Sodium Chloride-Water. ($t = 18^\circ.1$).¹

p .	d .	n .	R_1 .	R_2 .
1	1.0072	1.33525	0.3328	0.2239
2	1.0145	1.33701	0.3321	0.2449
5	1.0362	1.34225	0.3303	0.2619
10	1.0733	1.35103	0.3271	0.2659
15	1.1114	1.35994	0.3238	0.2672
20	1.1510	1.36897	0.3205	0.2669
25	1.1922	1.37824	0.3172	0.2671

Mean, 0.2568

Table IV.—Sodium Iodide-Water. ($t = 18^\circ$).²

p .	d .	n .	R_1 .	R_2 .
10	1.082	1.34445	0.3183	0.1779
20	1.179	1.36760	0.3118	0.2234
30	1.294	1.39075	0.3019	0.2283
40	1.432	1.42890	0.2925	0.2304

Table V.—Sodium Nitrate-Water. ($t = 22^\circ.8$).

p .	d .	n .	R_1 .	R_2 .
16.9	1.1178	1.35183	0.3147	0.2206
44.4	1.3580	1.38538	0.2838	0.2187

Mean, 0.2197

¹ Schütt: Z. physik. Chem., 9, 351.

² Bender: Wied. Ann., 39, 90.

Table VI.—Sodium Carbonate-Water. ($t = 20^{\circ}.5$).

p .	d .	n .	R_1 .	R_2 .
1.42	1.0151	1.33624	0.3312	0.1438
2.80	1.0291	1.33944	0.3298	0.1793
6.73	1.0715	1.34771	0.3245	0.1983
12.7	1.1379	1.34990	0.3154	0.1878

Table VII.—Potassium Chloride-Water. ($t = 20^{\circ}$).

p .	d .	n .	R_1 .	R_2 .
5	1.03250	1.33975	0.3291	0.2369
10	1.06580	1.34650	0.3250	0.2449
15	1.10036	1.35368	0.3214	0.2502
20	1.13608	1.36127	0.3171	0.2499
24	1.16568	1.36960	0.3171	0.2638

Mean, 0.2491

Table VIII.—Potassium Bromide-Water. ($t = 20^{\circ}$).

p .	d .	n .	R_1 .	R_2 .
5	1.037	1.33900	0.3269	0.1939
10	1.070	1.34515	0.3226	0.2206
15	1.116	1.35178	0.3152	0.2086
20	1.159	1.35875	0.3096	0.2124
25	1.207	1.36628	0.3034	0.2119
30	1.256	1.37418	0.2979	0.2051

Mean, 0.2087

Table IX.—Potassium Iodide-Water. ($t = 20^{\circ}$).

p .	d .	n .	R_1 .	R_2 .
5	1.038	1.34008	0.3276	0.2079
10	1.078	1.34665	0.3216	0.2106
15	1.120	1.35460	0.3166	0.2180
20	1.166	1.36250	0.3109	0.2189
25	1.218	1.37145	0.3049	0.2179
30	1.271	1.38115	0.2998	0.2114
35	1.331	1.39125	0.2939	0.2119
40	1.396	1.40220	0.2881	0.2194
50	1.546	1.42835	0.2771	0.2202

Mean, 0.2151

Table X.—Potassium Nitrate-Water. ($t = 21^\circ$).

ρ .	d .	n .	R_1 .	R_2 .
1	1.0065	1.33426	0.3221	0.1539
2	1.0131	1.33521	0.3308	0.1789
3	1.0197	1.33600	0.3295	0.1874
4	1.0264	1.33690	0.3282	0.1914
5	1.0300	1.33773	0.3278	0.2119
10	1.0621	1.34240	0.3224	0.2187
15	1.0956	1.34735	0.3170	0.2207
20	1.1316	1.35263	0.3116	0.2224

Mean, 0.1923

Table XI.—Potassium Chlorate-Water. ($t = 20^\circ$).

ρ .	d .	n .	R_1 .	R_2 .
1	1.007	1.33426	0.3319	0.1339
1.5	1.010	1.33465	0.3313	0.1591
2	1.014	1.33505	0.3304	0.1589
4	1.026	1.33665	0.3281	0.1889
6	1.039	1.33833	0.3256	0.1953

Mean, 0.1672

Table XII.—Potassium Chromate-Water. ($t = 20^\circ$).

ρ .	d .	n .	R_1 .	R_2 .
3	1.0243	1.33973	0.3316	0.2573
4	1.0325	1.34187	0.3309	0.2489
5	1.0408	1.34401	0.3305	0.2659
10	1.0837	1.35525	0.3278	0.2729
15	1.1287	1.36715	0.3253	0.2763
20	1.1765	1.37940	0.3224	0.2754
25	1.2274	1.39233	0.3196	0.2767
30	1.2808	1.40525	0.3164	0.2661
35	1.3386	1.41985	0.3136	0.2671

Mean, 0.2674

Table XIII.—Lithium Chloride-Water. ($t = 20^\circ$).¹

ρ .	d .	n .	R_1 .	R_2 .
4.2	1.0243	1.34243	0.3343	0.3444
8.76	1.0508	1.35154	0.3345	0.3407
20.3	1.1191	1.37595	0.3359	0.3437
33	1.2040	1.40460	0.3360	0.3402

¹ Walter: Wied. Ann., 42, 511.

Table XIV.—Calcium Chloride-Water. ($t = 25^\circ$).¹

ρ .	d .	n .	R_1 .	R_2 .
33	1.143	1.37152	0.3250	0.3072
48	1.215	1.39411	0.3243	0.3137
83	1.398	1.44000	0.3140	0.3100

Table XV.—Cupric Chloride-Water. ($t = 15^\circ$).²

ρ .	d .	n .	R_1 .	R_2 .
5.17	1.0462	1.34790	0.3325	0.3068
38.2	1.4983	1.45490	0.3036	0.2545

Table XVI.—Copper Sulphate-Water. ($t = 20^\circ$).³

ρ .	d .	n .	R_1 .	R_2 .
5.58	1.0357	1.34381	0.3319	0.2881
15.05	1.0995	1.36267	0.3298	0.3065
16.79	1.1120	1.36619	0.3293	0.3068

Table XVII.—Zinc Chloride-Water. ($t = 26^\circ.5$).⁴

ρ .	d .	n .	R_1 .	R_2 .
23	1.2090	1.37515	0.0103	0.2324
36	1.3590	1.40222	0.2959	0.2305

Mean, 0.2315

Table XVIII.—Cadmium Chloride-Water. ($t = 15^\circ$).⁵

ρ .	d .	n .	R_1 .	R_2 .
14.8	1.140	0.35880	0.3174	0.2014
21.4	1.212	1.37160	0.3066	0.2056
30	1.321	1.38980	0.2951	0.2058
41.5	1.500	1.41978	0.2798	0.2040
57.5	1.831	1.47348	0.2585	0.2057

¹ v. d. Willigen: Arch. Mus. Teyler, 2, 209.² Walter: Loc. cit.³ LeBlanc: Z. physik. Chem., 4, 305.⁴ v. d. Willigen: Loc. cit.⁵ de Mynck: Wied. Ann., 63, 561.

Table XIX.—Cadmium Iodide-Water. ($t = 15^\circ$).¹

p .	d .	n .	R_1 .	R_2 .
3.3	1.029	1.33883	0.3292	0.1929
9.6	1.084	1.34846	0.3214	0.2039
13.2	1.111	1.35440	0.3189	0.2199
18.7	1.181	1.36405	0.3082	0.1977
24.2	1.246	1.37483	0.3008	0.1982
31.1	1.336	1.39033	0.2921	0.2001
35.5	1.405	1.40128	0.2856	0.1986
40	1.476	1.41379	0.2803	0.1999

Mean, 0.2014

Table XX.—Aluminium Chloride-Water. ($t = 18^\circ$).

p .	d .	n .	R_1 .	R_2 .
5	1.0360	1.34625	0.3342	0.3399
10	1.0733	1.35963	0.3351	0.3459
15	1.1124	1.37450	0.3367	0.3524
20	1.1537	1.39063	0.3386	0.3574
25	1.1967	1.40519	0.3389	0.3539
30	1.2421	1.42444	0.3417	0.3596

Table XXI.—Hydrochloric Acid-Water. ($t = 20^\circ.8$).²

p .	d .	n .	R_1 .	R_2 .
34.4	1.1660	1.41109	0.3526	0.3881

Table XXII.—Nitric Acid-Water. ($t = 20^\circ$).³

p .	d .	n .	R_1 .	R_2 .
14.1	1.079	1.35168	0.3259	0.2771
28.7	1.172	1.37235	0.3177	0.2788
40.5	1.250	1.38281	0.3062	0.2647
69.2	1.411	1.40390	0.2862	0.2671

Table XXIII.—Sulphuric Acid-Water. ($t = 18^\circ.3$).⁴

p .	d .	n .	R_1 .	R_2 .
4.46	1.0298	1.33862	0.3294	0.2439
30.1	1.2270	1.37009	0.3031	0.2323
71.8	1.6340	1.42466	0.2602	0.2307
89.0	1.8190	1.43669	0.2411	0.2270

¹ De Muynek: *Loc. cit.*² v. d. Willigen: *Loc. cit.*³ LeBlanc: *Loc. cit.*⁴ v. d. Willigen: *Loc. cit.*

Table XXIV.—Acetic Acid-Water. ($t = 19^\circ$).¹

p .	d .	n .	R_1 .	R_2 .
10.5	1.0143	1.33933	0.3345	0.3446
20.9	1.0278	1.34653	0.3371	0.3502
31.1	1.0403	1.35323	0.3395	0.3518
41.3	1.0508	1.35903	0.3417	0.3526
51.3	1.0589	1.36433	0.3440	0.3531
61.3	1.0653	1.36878	0.3461	0.3534
71.1	1.0696	1.37289	0.3486	0.3545
80.8	1.0707	1.37558	0.3508	0.3542
90.5	1.0675	1.37605	0.3522	0.3538
97.7	1.0560	1.37445	0.3546	0.3549

Mean, 0.3525

Table XXV.—Butyric Acid-Water. ($t = 20^\circ$).²

p .	d .	n .	R_1 .	R_2 .
94	0.9663	1.40211	0.4160	0.4209
96	0.9625	1.39946	0.4150	0.4182
98	0.9587	1.39949	0.4167	0.4184

Table XXVI.—Methyl Alcohol-Water. ($t = 20^\circ$).

p .	d .	n .	R_1 .	R_2 .
7.72	0.98456	1.33505	0.3403	0.4164
15.60	0.97301	1.33727	0.3466	0.4182
37.7	0.94106	1.34147	0.3607	0.4063
40.94	0.93461	1.34229	0.3662	0.4127
41.8	0.93187	1.34227	0.3672	0.4138
56.4	0.90302	1.34221	0.3789	0.4159
65.3	0.88312	1.34106	0.3862	0.4124
72.9	0.86475	1.33903	0.3920	0.4152
86.81	0.83127	1.33348	0.4011	0.4112
94.34	0.81112	1.33123	0.4083	0.4127
100	0.79500	1.32887		0.4136

Mean, 0.4123

¹ Landolt: Pogg. Ann., 117, 353.² Verschaffelt: Bull. Acad. Brux., 27, 77.

Table XXVII.—Ethyl Alcohol-Water. ($t = 25^{\circ}$).¹

p .	d .	n .	R_1 .	R_2 .
38.8	0.93189	1.35556	0.3815	0.4577
70	0.86853	1.36304	0.4181	0.4545
75	0.85150	1.36324	0.4266	0.4573
79.3	0.84097	1.36332	0.4320	0.4576
80	0.83925	1.35331	0.4209	0.4428
85	0.82674	1.35297	0.4269	0.4437
90	0.81359	1.35239	0.4331	0.4397
95	0.79992	0.35125	0.4391	0.4437
96	0.79700	1.36094	0.4528	0.4576
97	0.79405	1.36061	0.4541	0.4577
98	0.79110	1.36024	0.4554	0.4578
99	0.78815	1.35984	0.4565	0.4577
100	0.78510	1.35941		0.4578

Mean, 0.4577

Table XXVIII.—Glycerol-Water. ($t = 17^{\circ}.5$).²

p .	d .	n .	R_1 .	R_2 .
50	1.1251	1.3973	0.3531	0.3723
60	1.1526	1.4121	0.3567	0.3727
70	1.1800	1.4270	0.3618	0.3730
80	1.2027	1.4421	0.3662	0.3643
90	1.2342	1.4573	0.3705	0.3742
100	1.2600	1.4727		0.3723

Mean, 0.3713

Table XXIX.—Cane Sugar-Water. ($t = 17^{\circ}.5$).

p .	d .	n .	R_1 .	R_2 .
5	1.0200	1.34050	0.3338	0.3319
10	1.0404	1.34750	0.3340	0.3349
15	1.0614	1.35570	0.3351	0.3420
20	1.0832	1.36378	0.3358	0.3434
25	1.1059	1.37213	0.3356	0.3407
30	1.1295	1.38086	0.3372	0.3348

Mean, 0.3379

¹ Andrews: J. Am. Chem. Soc., 30, 353.² Strohmer: Organ. Ges. Vereins Rübenzucker-Industrie, 21, 1883.

The data recorded in the foregoing tables are plotted in Figs. II., III., and IV., the abscissae denoting percentage concentration and the ordinates specific refraction. An inspection of the diagrams shows that the curves may be divided into two classes: (1) those in which the experimentally determined specific refractions lie on the straight line joining the

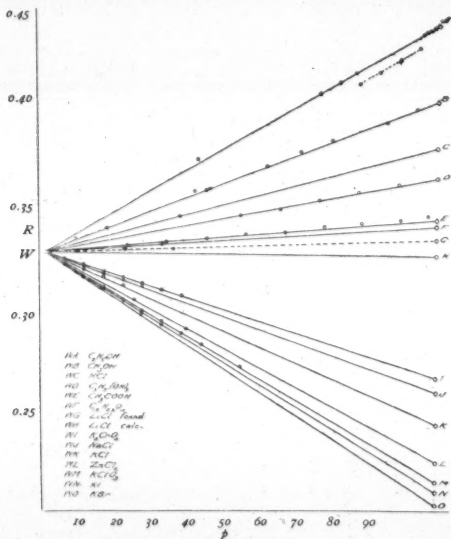


Fig. II.

specific refractions of pure solvent and solute; (2) those in which the experimentally determined specific refractions do not lie on this line. All of the solutes belonging to the first class are anhydrous, whereas the solutes of the second class either crystallize from solution with water of crystallization or are known to possess marked affinity for water. In plotting the data for hydrated solutes dotted lines have been employed.

For example, in Fig. IV., WD represents the calculated line for sulphuric acid, while the dotted line WK is that actually found.

In the case of cadmium iodide there is marked disagreement between the observed and calculated values of R_2 but

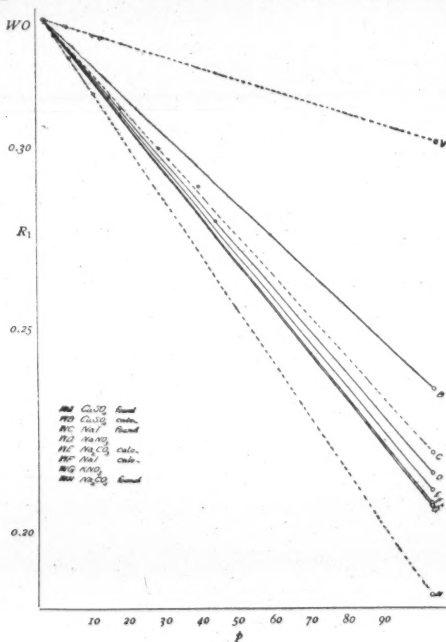


Fig. III.

we do not feel warranted in drawing any conclusions from this until the measurements have been repeated.

As has already been pointed out by Andrews,¹ there is a singular break in the refractive index-concentration curve

¹ Loc. cit.

In Table XXX. is given the value of the specific refraction as calculated from refractive equivalents for the anhydrous solute (R_a), for the hydrated solute (R_h), and also the experimentally determined value (R). In the fifth column the difference between the calculated and determined value is recorded.

Table XXX.

Solute.	R_a (calc.).	R_h (calc.).	R (found).	Diff.
NaCl	0.2649		0.2675	-0.0026
NaI.2H ₂ O	0.2136	0.2303	0.2263	+0.0040
NaNO ₃	0.2211		0.2200	+0.0011
Na ₂ CO ₃ .10H ₂ O	0.2169	0.2692	0.1900	+0.0792
KCl	0.2486		0.2475	+0.0011
KBr	0.2079		0.1950	+0.0129
KI	0.2144		0.2195	-0.0051
KNO ₃	0.2131		0.2200	-0.0069
KClO ₃	0.2198		0.2075	+0.0123
K ₂ CrO ₄	0.2722		0.2757	-0.0035
LiCl.2H ₂ O	0.3341	0.3184	0.3425	-0.0241
CaCl ₂ .6H ₂ O	0.2828	0.2913	0.3100	-0.0187
CuCl ₂ .2H ₂ O	0.2444	0.2561	0.2538	+0.0023
CuSO ₄ .5H ₂ O	0.2424	0.2632	0.3050	-0.0418
ZnCl ₂	0.2294		0.2287	+0.0007
CdCl ₂ .2H ₂ O	0.1885	0.2067	0.2063	+0.0004
CdI ₂	0.1698		0.1846	-0.0148
AlCl ₃ .6H ₂ O	0.2981	0.2989	0.3550	-0.0561
HCl	0.3889		0.3882	+0.0007
HNO ₃	0.2381		0.2700	-0.0319
H ₂ SO ₄	0.3041		0.2305	+0.0735
CH ₃ COOH	0.3525		0.3550	-0.0025
<i>n</i> -C ₃ H ₇ COOH	0.4123		0.4123	0.0000
CH ₃ OH	0.4122		0.4122	0.0000
C ₂ H ₅ OH	0.4506		0.4506	0.0000
C ₃ H ₇ (OH) ₃	0.3738		0.3720	+0.0018
C ₁₂ H ₂₂ O ₁₁	0.3491		0.3537	-0.0046

Reference to Table XXX. shows that there is approximate agreement between R_h and R for NaI.2H₂O, CuCl₂.2H₂O, and CdCl₂.2H₂O, but that for other hydrated solutes marked differences exist. For the three salts named above it is possible to calculate quite closely the number of molecules of water of crystallization from the specific refractions of solute and solvent.

Let Rm denote the molecular refraction of the solute, the molecular refraction being the product of the specific refraction of the solute, R , and its molecular weight m , and let n be the number of molecules of combined water.

Then

$$r = \frac{Rm + 5.4 n}{m + 18 n} \quad (3),$$

where r is the specific refraction of the solute determined by experiment and 5.4 is the molecular refraction of water.

Solving (3) for n we have

$$n = \frac{(R - r) m}{18 r - 5.4} \quad (4).$$

Applying equation (4) to sodium iodide, cupric chloride, and cadmium chloride we find for n the values, 2.2, 2.0, and 2.4, respectively. Attempts to apply the equation to other solutes having a greater number of molecules of water of crystallization or having marked affinity for water, as sulphuric acid, have been unsuccessful, in several cases n being affected with a negative sign.

The results of this investigation may be summarized thus:

(1) Aqueous solutions may be divided into two classes:

(a) Those in which the specific refraction of the solute as calculated from its solutions agrees with its specific refraction as computed from the refractive equivalents of its constituent elements.

(b) Those in which the specific refraction of the solute as calculated from its solutions does not agree with the specific refraction as computed from refractive equivalents.

(2) All solutes belonging to division (a) are anhydrous; all solutes belonging to division (b) are hydrated.

(3) An attempt was made to derive a formula for calculating the degree of hydration, but as yet no satisfactory quantitative expression can be given.

We propose to continue the investigation of the relation of specific refraction to hydration.

ACTION OF RADIUM EMANATION ON SOLUTIONS OF COPPER SALTS.¹

BY MME. CURIE AND Mlle. GLEDITSCH.

Ramsay and Cameron announced a year ago, in various publications, that they had observed the production of the alkali metals and of lithium in solutions of copper salts subjected to the action of radium emanation. They concluded that in the presence of the emanation the metal copper suffers a *degradation* into elements of the same family and of lower atomic weights: potassium, sodium, lithium.²

These important results attracted much attention and it seemed desirable to repeat the experiments in laboratories which possess a sufficiently large quantity of radium.

They carried out their experiments as follows: A solution of a copper salt (sulphate or nitrate) was placed in a glass bulb into which a considerable quantity of emanation was introduced and allowed to destroy itself spontaneously. Then the copper was removed, the solution remaining evaporated to dryness, and the residue examined. The same operations were carried out with a solution of the same copper salt but which had not been subjected to the action of the emanation. The experiments were repeated several times. The residue consisted principally of a sodium salt (with a little potassium and calcium); in the four experiments described, where the emanation was allowed to act on the solution, the presence of lithium was observed by means of the spectroscope; in the blank experiments the residue was appreciably smaller, and no lithium was detected. Ramsay and Cameron attempted to determine the amount of lithium present, and they concluded that the residue, which weighed 1.67 mg. for 0.27 gram copper employed (0.815 gram copper nitrate), contained about 0.00017 mg. lithium, while in the corresponding blank experiment the residue weighed only 0.79 mg.³

¹ Compt. rend., **147**, 345 (1908).

² Nature July, 1907; J. Chem. Soc., Sept., 1907; Compt. rend., 1908; Arch. Genève, April, 1908; etc.

³ This quantity of metallic lithium does not correspond to the amount indicated by the mixture of sodium and lithium salts which were employed for comparison, and there must be a typographical error which we have been unable to locate.

We have attempted to repeat the experiments with the greatest possible care. The experiment is, in fact, a delicate one and involves several sources of error, the most serious of which is the use of a glass vessel, as Ramsay himself pointed out.

Our preliminary experiments showed that it is extremely difficult to obtain chemical products free from lithium. It is found in distilled water, in almost all reagents; if a reagent which does not contain any is allowed to stand in a glass vessel, it will after a time show traces of the metal. The following experiment was carried out: Two hundred and fifty cc. of water which had been distilled from a platinum retort and kept in a platinum bottle left no visible residue when evaporated in a platinum dish, and the last drop resulting from the concentration did not give the lithium spectrum; but water obtained in the same way, when kept in a glass vessel for 24 hours, left, on evaporation, a small residue consisting principally of a sodium salt, but containing also a trace of lithium.

It seemed to us indispensable to replace glass by some other material. We found that it is equally dangerous to employ quartz, a material which Ramsay is now using, because commercial quartz vessels contain lithium. We treated a fragment of an opaque quartz vessel and a piece of transparent quartz tubing with hydrofluoric acid free from lithium; in the residue the presence of an appreciable quantity of lithium could be detected; transparent quartz contains much more than opaque quartz. We then decided to use platinum vessels.

The apparatus which we employed consists of a horizontal platinum cylinder, 7.5 cm. long and with an external diameter of 1.5 cm.; this cylinder is provided at one end with a small vertical platinum tube through which the solution can be introduced. The small tube has a platinum cover which protects the solution but is not water-tight. A glass tube provided with a side tube and stopcock is sealed on the outer side over the platinum tube. The solution is introduced into the apparatus by means of a platinum siphon and is re-

40
8

moved in the same way and never comes in contact with glass.

The water and acids necessary for the experiment were distilled in a platinum retort and kept in bottles made of the same metal; we had found, in fact, that all these reagents contained lithium, especially the sulphuric acid. After the purification described above, we were no longer able to detect the presence of lithium in the residue from the evaporation of 80 cc. of nitric acid, 25 cc. of sulphuric acid, 25 cc. of hydrofluoric acid, and 250 cc. of water.

As Ramsay pointed out, pure commercial copper salts contain appreciable quantities of lithium. We tried various processes of purification: repeated precipitation with hydrogen sulphide, electrolytic deposition of the copper, fractional crystallization; finally we used copper sulphate which had been recrystallized many times in a platinum vessel, pure water being used for each successive solution. This treatment is at first very efficacious, but on the other hand it is very difficult, if not impossible, to remove the last traces of lithium. When we discontinued the purification we could with great difficulty detect lithium in the residue from 50 grams of copper, but not at all in the residue from 2 grams of the salt.

The emanation was supplied by a solution containing 0.19 gram of radium (0.25 gram of radium chloride). It was first condensed in a spiral immersed in liquid air, then aspirated into the platinum apparatus. To determine with certainty the amount of emanation which was introduced, we measured the penetrating radiation of the apparatus by comparing it with that of a phial containing a known quantity of radium. For this purpose we employed a specially constructed condenser with large plates.

Two experiments, which were in all respects analogous, were performed. We introduced into the apparatus about 7 cc. of a solution of pure copper sulphate. The liquid had a relatively large free surface compared to its volume. The apparatus was then sealed in the flame. The emanation was introduced at various intervals; in order to insure its solution the liquid was stirred by inclining the apparatus, which was

placed in melting ice; this operation was frequently repeated. The weights of copper used were 0.26 and 0.14 gram, respectively. The whole amount of emanation introduced corresponded in both cases to the saturated emanation of 0.37 gram radium; the quantity which was destroyed in the apparatus was somewhat less; it corresponded to the saturated emanation of 0.27 gram radium. When the experiment was thought to be completed, the solution was transferred from the apparatus to a platinum crucible and a few drops of nitric acid were added. Into the crucible was introduced a platinum electrode, on which the copper was deposited. The solution freed from copper was evaporated to dryness in the crucible and the temperature raised just high enough to expel the sulphuric acid; the residue was dissolved in a few drops of water and treated with hydrogen sulphide to remove the traces of copper which were still present. The liquid was filtered through a little platinum funnel into a platinum lid of known weight and evaporated to dryness at a very low temperature. The small residue was weighed.

Seven cc. of a solution of pure copper sulphate which had not been subjected to the action of the emanation were treated in the same way. The residues finally obtained were examined in the spectroscope. In the experiments in which the emanation had been used, the residues weighed 0.0004 and 0.0005 gram, respectively, and in the blank experiments 0.0003 and 0.0002 gram.

We may mention that the quantity of copper employed is nearly the same as that used by Ramsay. The amount of emanation which we utilized is also approximately the same (1.85 cubic mm., according to Ramsay's basis of evaluation). Nevertheless, the residue finally obtained was much smaller.

The spectroscopic examination showed that this residue contained principally sodium and a little potassium; the presence of lithium could not be detected. An experiment made with mixtures of sodium and lithium sulphates showed that the red line of lithium could still be detected, although with difficulty, in a mixture containing 10,000 parts of sodium sulphate to 1 part of lithium sulphate, and that the same line

could easily be seen with a mixture containing 3,000 parts of sodium sulphate to 1 part of lithium sulphate. Consequently the quantity of the metal lithium which could be present was less than 0.000006 mg.

With the same quantities of copper and emanation, Ramsay and Cameron found 0.00017 mg. lithium. If, owing to a typographical error, this value should represent lithium chloride, the quantity of the metal lithium would still be equal to 0.00003 mg.

The residue which we obtained was, in every case, much smaller than that obtained by Ramsay and Cameron, and this probably results from the substitution of platinum for glass in our experiments. The differences in the weights of the residues obtained by us in the experiments in which the emanation had been used and in the blanks is very small (0.1 to 0.3 mg.); it is probably due to the fact that, in the former, traces of foreign matter are introduced with the emanation. In the most satisfactory of Ramsay and Cameron's experiments, this same difference is equal to 0.88 mg., and we believe that it may be attributed to the more energetic action of the solution on the glass in the presence of the emanation.

The following control experiment was carried out: Into a solution of copper sulphate containing 0.27 gram of copper, we introduced a quantity of lithium sulphate corresponding to 0.00017 gram of lithium chloride; this solution was then treated in the same manner as in the experiments described above. With the residue finally obtained it was very easy to see the red lithium line, which proves that the lithium was not lost during the course of the experiment.

In conclusion, we may say that we have been unable to confirm the results of Ramsay and Cameron. It is evidently impossible to affirm that no trace of sodium or lithium was formed in the experiment; we believe, however, that the formation of these elements cannot be considered an established fact.

REVIEWS.

A COURSE OF PRACTICAL ORGANIC CHEMISTRY. By T. SLATER PRICE, D.Sc., Ph.D., F.S.C., Head of the Chemical Department of the Birmingham Municipal Technical School; Formerly Senior Lecturer on Chemistry at the University of Birmingham, and DOUGLAS F. TWISS, M.Sc., A.S.C., Lecturer on Chemistry at the Birmingham Municipal Technical School. London, New York, Bombay, and Calcutta: Longmans, Green & Co. 1907. pp. 239. Price, \$1.20.

This text-book is intended to meet the requirements of the "Board of Education" syllabus for Practical Organic Chemistry. The authors say: "We have endeavored to arrange the course so that the student will get a completely satisfactory practical acquaintance with organic chemistry." The preparations have been selected with care and the descriptions are clear. There can be no doubt that any student who conscientiously follows the course here laid down will acquire a good knowledge of the subject. Whether the knowledge will be "completely satisfactory" will depend upon what is expected.

In addition to the directions for preparations there are given many "tests" and schemes for the identification of compounds. Chapter XIV. treats of the determination of the molecular weight (1) by chemical methods, (2) by physical methods. Chapter XV. treats of special quantitative work; and Chapter XVII. gives a general scheme for the detection of an organic compound.

The book appears to be well adapted to the purposes for which it has been written.

I. R.

LABORATORY EXERCISES IN PHYSICAL CHEMISTRY. By FREDERICK H. GETMAN, Ph.D., Lecturer in Physics, Columbia University, formerly Carnegie Research Assistant, Johns Hopkins University. Second Edition, Revised, First Thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1908. pp. 285. Price, \$2.00.

The appearance of the first edition of this admirable laboratory manual was duly referred to in *THIS JOURNAL*.¹ The prompt appearance of the second edition shows that the book has been favorably received. Some additions have been made in this new edition, as is shown by the following lines taken from the preface: "The author would call attention to the insertion of a chapter on thermostats and to the enlargement of the chapters treating of electromotive force, solubility, and chemical dynamics.

"A brief outline is given of methods for the measurement

¹ 32, 296 (1904).

of radioactivity, and several other chapters have been modified to conform with modern laboratory requirements."

The work presents a truly scholarly appearance, which is more than can be said of many scientific books. The reviewer must, however, object to the use of "foreward" in English. In the next edition, which will doubtless be quickly demanded, let us hope that the author will remove this trifling blemish.

H. C. J.

DIE ENTWICKELUNG DER LEUCHTGASERZEUGUNG SEIT 1890. Sammlung chemischer und chemisch-technischer Vorträge. Band XII., Hefte 7-8. Von DR. W. BERTELSMANN. Stuttgart: Ferdinand Enke. 1907. pp. 90. Price, 1.2 Marks.

As would be expected, the book deals largely with the apparatus employed, discussing first the horizontal retorts and the devices for mechanically charging and discharging them; this is followed by a description of the various inclined and vertical retorts and the coke ovens. About one-third of the book is devoted to the manufacture of water gas and mixed gases. Finally other methods of gas manufacture are discussed; the Dinsmore, the injection of tar and alcohol into the retorts, and the process of Sabatier in which methane is made by passing carbonic oxide and hydrogen over hot iron.

The statistics contained in the book are valuable and it will be of interest to all those having to do with the manufacture of gas.

A. H. GILL.

THE DATA OF GEOCHEMISTRY. By FRANK WIGGLESWORTH CLARKE, Washington: U. S. Geological Survey, Bull. 330. 1908. pp. 716.

The appearance of this work, bringing together the scattered information gathered by many investigators working with different ends in view, emphasizes the fact that there is developing another series of problems in a field lying between the well-marked sciences of chemistry and geology. The field demands the simultaneous application of the mental methods of exactness developed in chemical work and of convergent approximation necessary in the study of more or less irreducible complexes such as the earth studies furnish. It need not seem strange, therefore, if summaries like the present one occasion misunderstanding or inappreciative criticism on the part of workers accustomed to employ but a single viewpoint. The work is issued, not as an exhaustive monograph on the subject, but rather as a critical summary and guide to the literature. The purpose appears to be the collection of the data, the formulation of problems, and the restatement of old facts in modern terminology. To this

end the author has compiled the chemical data concerning the earth as a whole, its waters—oceanic, lacustrine, and fluvial; its rocks, their minerals, origin, and alteration; the metallic ores; and the natural hydrocarbons. The wealth of material brought together is made accessible by an excellent index of fully 5000 entries. The summaries are clear, concise, and critical, and the most recent literature is unusually well represented.

Among the many interesting topics discussed, attention may be called to the large amount of recent work in the study of the physical-chemical conditions surrounding the formation of the igneous rocks, their magmas, minerals, and alterations. The summaries seem to indicate that the investigators now generally accept the view that rock magmas are solutions under great pressures and at high temperatures, behaving essentially like other solutions; that they conduct electricity and may be at least partially ionized. There is, however, little knowledge or agreement as to the composition of the ions or the conditions especially helpful to dissociation. It is also agreed that in some instances, at least, the components of the magmas form eutectics but these are unknown or unproven. The components are probably more than three and each is a complex silicate. Moreover, the composition of the eutectics appears to be different at different temperatures and pressures and to be in some way variable with the bulk composition of the magma.

It likewise is generally accepted that the chemical composition of magmas possess certain characteristic differences and that the rocks produced from a given magma may differ widely in composition while retaining certain common characteristics. To explain these phenomena many hypotheses have been proposed and these may be grouped as follows:

Differences in composition due to mixing:

- a. Two or more magmas of different composition.
- b. Magmatic assimilation of the rock intruded.

Differences in composition due to the separation of a homogeneous magma into parts through

- a. Concentration of the dissolved substances in the cooler parts of the reservoir.
- b. Separation of the magma into layers by liquation.
- c. Separation by fractional crystallization, gravitational adjustment and refusion due to
 - (1) Variation in pressure and temperature, or
 - (2) Excess of components over eutectics.

The widely divergent views are held by prominent workers to-day but the drift of opinion appears to be that all causes

may be competent and that fractional crystallization is the most efficient. No final solution is likely to be reached without a great increase in knowledge of solutions at high temperatures and under high pressure, their components, eutectics, and conductivities; and the conditions, chemical and physical, determining the formation of a given silicate complex from a silicate melt.

E. B. MATHWES.

LEAD REFINING BY ELECTROLYSIS. By ANSON GARDINER BETTS. New York: J. Wiley & Sons. 1908. pp. ix + 394. Price, \$4.00.

In the desilverization of argentiferous lead the Parkes process has so far occupied the whole field, if we except the Luce-Rozan process in operation some twenty years ago at Eureka, Nev. The different attempts at electrolytic refining all proved a failure until the invention of the Betts process, in which an aqueous solution of lead fluosilicate acidified with hydrofluoric acid is the electrolyte. From the argentiferous lead forming the anode, copper, antimony, bismuth, arsenic, silver, and gold go into the anode slime; zinc, iron, nickel, and cobalt go into solution; and lead and tin are deposited on the lead cathode. In the presence of tin this would have to be removed by the usual fire process before electrolysis.

The present book is a record of the large amount of research, mainly by the author, which preceded the erection of a working plant to make a commercial test; a discussion of the practical features; and a brief description of the two plants in operation.

The first chapter reviews critically the different electrolytes that have been recommended for refining lead and gives full details regarding the successful acid lead fluosilicate. The question of slime treatment is discussed very elaborately and gives a variety of methods. The reason for this probably is the fact that this part of the process has not yet been worked out to complete satisfaction. The space given to the electrolytic refining of doré silver is a great deal too small, even if it is foreign to the main purpose of the book. Discussions of practical details of construction, of operation and of cost forms a most valuable chapter. The descriptions of the works at Trail, B. C., and Grasselli, Ind., are probably as complete as business considerations make this possible at present. Whether the new process will be able to compete with the established Parkes process, as is held by the author, is still an open question.

Taking the book as a whole, it is written by a man who is a master of his subject, and who has tried to the best of his

ability to give an unprejudiced account of all that can be made known at present about the only successful method of refining argentiferous lead electrolytically. H. O. HOFMAN.

PRACTICAL METHODS FOR THE IRON AND STEEL WORKS' CHEMIST. By J. K. HRESS, PH.C., Chief Chemist for the Carnegie Steel Co. Easton Pa.: The Chemical Publishing Co. pp. 60.

This book contains descriptions of the methods used by the author in the analysis of iron and steel, and all the various materials employed in their manufacture.

The methods are those ordinarily adopted in large plants and are selected more for the facility and speed of their execution than for the accuracy of the results obtained by their use.

In his introduction, the author states that the work is intended for the inexperienced chemist, and to accustom him to their use, he mars the appearance of his text by the general use of formulae and symbols. For those who are not only inexperienced but ignorant, he provides a table with the names and formulae of the various reagents and salts. The reactions on which the methods are based are, however, omitted, probably to avoid mental confusion in the reader, who, being supposed to have no knowledge of the principles of chemistry, can follow the directions with an easy mind.

The substance of the text is entirely in keeping with its appearance. The ordinary rules of English grammar are generally disregarded. The article and the impersonal pronouns are usually omitted, while the use of the passive form of the indicative and the imperative in the same sentence is not uncommon. Occasionally this disregard of rules is actually misleading, as in the sentence "a slag sample so kept is not reliable only for a short time." Such expressions as "let stand," "take about to dryness," "let boil," "doing steel," "doing a manganese," are found on every page, while in one instance, the neophyte is warned not to make a solution "too neutral."

A. A. BLAIR.